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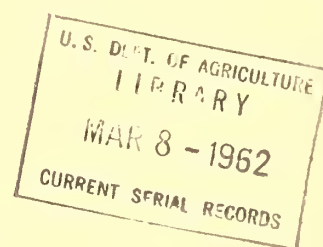
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Marketing Research Report No. 523

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**Predicting  
Quality  
of Stored  
COTTONSEED  
OILS**



Agricultural Marketing Service  
Market Quality Research Division  
U.S. DEPARTMENT OF AGRICULTURE

## PREFACE AND ACKNOWLEDGMENTS

The study on which this report is based is part of a comprehensive research project on quality evaluation and development of objective measurements of quality factors to improve the efficiency in the marketing of agricultural products.

A preliminary report on the storage of cottonseed oils, "Evaluating Refined Cottonseed Oils in Storage," was presented at the 1958 spring meeting of the American Oil Chemists' Society and is published in the Journal of the society, Volume 36, No. 1, January 1959. A further report, "Evaluating Refined Cottonseed Oils Under Various Conditions of Storage in Drums," was made at the 1959 fall meeting of the society. A summary of this, the final report on cottonseed oils, was presented at the 1961 spring meeting of the society.

Other studies in the project pertaining to the storage of vegetable fats and oils are reported in Marketing Research Report No. 384, "Evaluating the Market Quality of Commercially Stored Linseed Oil," U. S. Department of Agriculture, Agricultural Marketing Service, Washington, D. C. This report has also been published under the same title in the Journal of the American Oil Chemists' Society, Volume 36, No. 10, October 1959.

Similar studies of soybean oils are in progress at the present time.

The evaluation of the several samples of the cottonseed oils for "flavor and odor" by those participating members of industry proved very helpful.

The careful attention to sampling and temperature recording of the oils at the Southern Utilization Research and Development Division of the Agricultural Research Service at New Orleans by A. J. Crovetto, under the supervision of E. A. Gastrock, aided in procuring these data. The helpful assistance at the Western Utilization Research and Development Division of the Agricultural Research Service at Albany, California, on the part of P. W. Kilpatrick under the supervision of W. D. Ramage is also appreciated.

The preparation and evaluations of the shortenings by the Research Department of the Wesson Oil and Snowdrift Company at New Orleans, through the cooperation of P. A. Williams, and under the supervision of the late Dr. H. D. Royce, were most helpful in this important phase of the study. This company also provided a field tank of refined oil for temperature observations during 1958, through the courtesy of the late J. H. Brawner. The assistance of W. R. Kittredge and G. H. Bonnington is also acknowledged.

R. T. Doughtie, Jr., in charge of cottonseed grading of the Cotton Division, AMS, USDA, in Memphis, Tennessee, advised on the evaluation of refined cottonseed oils graded below prime bleachable summer yellow.



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## SUMMARY AND CONCLUSIONS

Given the initial characteristics of moisture and volatile matter, free fatty acids, refined and bleached colors, peroxide value (refined oils) and refining loss (crude oils), it is possible to predict probable changes of these characteristics during various periods of storage. These predictions are based on the methods and formulas developed in the project and on the proposed conditions of storage.

Oil in large vertical cylindrical tanks, filled to capacity, with limited access to air, and stored in cool areas should undergo minimum change in characteristics. Crude oils should be stored under conditions that minimize change. Changes in the characteristics of refined oils may increase or decrease the value of the oils, depending upon the initial characteristics of the oils and the storage conditions.

Changes in the characteristics of cottonseed oils during storage were related to a time-temperature factor. Refined oils were stored up to 3 years in 45 field tanks; refined and crude oils were stored up to 4 years in 74 drums. Forty-four field tanks contained oil acquired by the Commodity Credit Corporation during the price-support programs of the early 1950's. The drums were part of a study set up to compare field tank storage with experimentally controlled storage.

Refined cottonseed oils which did not meet specifications of the Trading Rules of the National Cottonseed Products Association for moisture and volatile matter before storage, met specifications after storage in field tanks and drums for various times at different temperatures. All refined and crude oils approached a constant moisture content during storage.

The free fatty acids in the oils increased during storage and the rate of increase was related to the initial free fatty acids content. However, only refined or crude oils having rather high initial free fatty acid content would be expected to exceed specifications even after unusually long storage.

The color of all refined oils in tanks and drums decreased during storage, upgrading several of the oils based on trading rules specifications. Rate of color decrease depended on initial color, quantity of oil, and location and type of storage. The color of most of the crude oils stored in drums increased and the differences in rates of change among oils extracted from seed by five different methods were significant.

Most of the refined oils changed in bleachability during storage, depending on the relationship of initial bleached color to initial refined color. The bleachability of crude oils in drums decreased during storage, and the decrease was significantly related to the extraction method.

When tested objectively for peroxide value and by the active-oxygen method (AOM) for fat stability, all refined oils in drums, and in the few tanks tested, decreased in "resistance to oxidation" and the amount of decrease

varied with storage conditions. Peroxide values of the stored refined oils were significantly related to fat stabilities, before and after bleaching and deodorizing. These objective tests differentiated among the various storage conditions; however, results of the peroxide value test appear to vary less than the AOM fat stability test. The AOM fat stability of crude oils did not appear to decrease or the peroxide value increase during storage.

Only one grade of refined oil, prime bleachable summer yellow, is recognized in market quotations. Oils below this designation are subject to negotiation in the trade; opinions from industry indicate that discounts for choice or prime summer yellow amount to about 50 points per pound. Summer yellow oils may be further discounted another 50 points. (One hundred points equal one cent.)

Storage conditions that maximize change in characteristics may cause some refined oils to be upgraded according to the rules. However, the buyer can claim "off-flavor and odor" (which claim may be based on high peroxide value even though this test is not a requirement in specifications), and the price of these oils could be subject to barter.

Several members of industry judged a few of the refined oils to be "off in flavor and odor" after 28 and 39 months' storage. However, the average discounts judges made were negligible, and there was little relationship between the number of times an oil was judged "off in flavor and odor" and the age of the oil, type of storage conditions, or the objective analyses for "keeping quality." Standard shortenings made from four of the oils stored 4 years and from one oil stored 1 1/4 years of varying "quality" (according to peroxide value and AOM fat stability) were judged to have choice flavor and good odor when compared with a shortening made from fresh oil. All six of the shortenings were further judged to have good flavor and odor after 8 months' storage at room temperature under household conditions.

## PREDICTING QUALITY OF STORED COTTONSEED OILS

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### INTRODUCTION

The vegetable-oil industry rarely stores refined cottonseed oils beyond the season's requirements. Crude cottonseed oils are usually refined in a matter of days after extraction from seed to prevent ensuing quality deterioration. Information on quality changes during longer storage of refined and crude cottonseed oils is important to the industry and to the Government.

If oils could be stored longer without substantial change in quality or value, more orderly and efficient marketing would be possible. Furthermore, better knowledge as to the effect of storage on oils would contribute to the production of better quality oils.

Such an investigation may indicate the grade and quality of oil best suited for storage and the best types, sizes, and locations of tanks. Based on initial quality characteristics of the oil, probable changes in these characteristics under various periods and conditions of storage might be predicted. Objective tests of stored oils might indicate past conditions and length of storage. This report shows methods by which such tests may be done.

Data have been procured from three sources: The commodity examination reports of the Commodity Credit Corporation during the price-support programs of the early 1950's when large quantities of refined cottonseed oils were stored for periods up to 3 years; the examinations of crude and refined cottonseed oils stored experimentally in drums for periods up to 4 years; and, examinations over a 9-month period of an experimental field tank of refined oil.

### OBJECTIVES

Primary objectives of this study were: 1. Determination of the extent of changes in quality and value of crude and refined cottonseed oils stored under commercial conditions for longer periods than are customary in industry; 2.

evaluation of present industrial methods of measuring the quality of cottonseed oils; and 3. determination of the best methods as to sizes, types, and locations of field tanks for storing oils in order to maintain quality.

## METHODS AND PROCEDURES

Basic information needed to carry out these objectives consists fundamentally of data obtained from various objective and subjective tests, and from examinations of samples of oil taken from the field tanks in the CCC operations, and of samples taken from the experimental drums during specified storage periods. Because oils from several sources were stored at several locations, under widely different atmospheric conditions, relating these data to a common factor in order to compare field tanks with field tanks, drums with drums, and tanks with drums was an initial problem of the project.

### The Time-Temperature Factor

Changes in the various quality characteristics of oils during storage were assumed to depend upon temperature and time of storage, but various other storage conditions were considered to be possible contributing factors. Furthermore, based on previous studies <sup>1/</sup> of deterioration in foods during storage, it was assumed that as temperature increases, deterioration accelerates. Also, there would be little or no change when the oil was not in a liquid state.

The following bases determined the time-temperature factor which was used in the present project:

1. There were no significant changes in any of the quality characteristics of the oils during storage when the mean temperature of the oils, either in the drums or in the field tanks, was below 50° F.
2. The mean temperature of the oils in the drums and in the field tanks over a period of time was not significantly different from ambient temperatures, provided the drum or tank was situated on the ground and exposed to outside atmospheric conditions.
3. Samples of oil taken from the center of drums and tanks were at the mean temperature of all the oil at the time of sampling.
4. Differences in characteristics were not significant between samples of the oils taken at the same time from different points within the same tank or drum.
5. When an accelerated rate of 0.1 unit for every 5° F. increase in temperature (above 50° F.) was adopted, six drums of the same oil under the

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<sup>1/</sup> Time-temperature Tolerance Studies of Frozen Foods. West. Reg. Res. Lab., ARS, U. S. Dept. Agr., Albany, Calif.



same type of storage conditions, for periods up to 3 years, at three locations (Beltsville, Md.; New Orleans, La.; and Albany, Calif.) each had the same rate of change in quality characteristics during each storage period.

Table 1 gives the time-temperature units, based on official U. S. Weather Bureau reports for 1959, for 10 locations where most cottonseed oils are generally stored. Annual differences were not significant when related to the data in the project.

### Sampling Methods

All samples from field tanks in the CCC operations were taken with a bomb sampler by Government inspectors, following methods of the AOCS C-147. 2/

The extent of any free water, foots (settlings of non-oil constituents), or both was determined in the oil in each tank. This portion, usually about 1 foot at the bottom of the tank, is called the "bottom." A single sample taken from this portion in each tank is called the "bottom" sample. Oil above the bottom in the tank is called the "balance." Several samples were taken, at 1- to 3-foot intervals, of the balance to make up a composite known as the "balance" sample.

The Government sampler also reported the weight (warehouse records), depth of the oil and, in several cases, temperature of the oil. Dimensions and capacities of the tanks were also reported.

Records were available for 44 tanks of refined oil stored at Los Angeles, Calif.; Houston, Tex.; and New Orleans, La.; for periods ranging from 1 to 3 years. Each tank was sampled from 6 to 17 times at approximately regular intervals. Very few of the bottom samples indicated the presence of stearine. Very few temperatures of the balance samples were below 60° F.

Oil stored in drums was sampled by glass pipette at the center of the oil through the top bung. Drums were set on end at a slight angle with asphalt flush to the top to allow for drainage of rain water.

Oil in drums was sampled about every 3 months, and generally when temperatures were above 60° F. From 10 to 16 samples were taken from each drum during periods up to 4 years. There were 38 drums of refined and 14 drums of crude oils stored at Beltsville, Md.; 8 drums of refined and 4 drums of crude oils at New Orleans, La.; 4 drums of refined and 4 drums of crude oils at Albany, Calif.; and 2 drums of refined oil at Bayonne, N. J. (the latter drums were stored only 15 months for comparison with the experimental field tank at this location).

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2/ American Oil Chemists' Society, Official and Tentative Methods. Chicago, Ill.

Table 1.--Time-temperature factors in accelerated hour-degrees (above 49° F.) for 10 areas 1/

Month:	Chicago, Ill.	N. Y., N. Y.	Cincinnati, Ohio	Washington, D. C.	Memphis, Tenn.	Oakland, Calif.	Dallas, Texas	Houston, Texas	New Orleans, La.	Los Angeles, Calif.
Jan.	0	5	43	75	188	508	287	432	441	815
Feb.	6	0	86	78	257	408	356	549	626	657
Mar.	72	28	177	222	494	685	625	803	808	905
Apr.	367	387	545	679	755	779	809	904	943	895
May	868	895	923	1,001	1,064	830	1,087	1,109	1,111	931
June	1,152	976	1,019	1,062	1,082	864	1,129	1,142	1,129	954
July	1,083	1,079	1,103	1,130	1,138	917	1,189	1,177	1,166	1,067
Aug.	1,129	1,100	1,119	1,157	1,160	930	1,231	1,179	1,183	1,048
Sept.	949	984	963	1,019	1,044	890	1,104	1,111	1,108	1,002
Oct.	440	732	611	794	856	913	918	1,033	1,048	972
Nov.	91	156	209	302	383	587	417	551	631	892
Dec.	50	58	109	130	288	423	483	612	618	812
Total:	6,207	6,400	6,907	7,649	8,709	8,734	9,635	10,602	10,812	10,950

1/ Calculated from U. S. Weather Bureau reports at local airports by grouping hour-degrees in increments of 5°, using a factor of 1.0 times the total hour-degrees of 50-54° as a base and increasing the factor by 0.1 for higher temperatures; such as, total hours of 55-59° times 1.1, total hours of 60-64° times 1.2, etc. There were no significant differences in using the temperatures of the nearest Bureau location as compared to the temperature at the exact location of storage; namely, between Bayonne, N. J. and New York International Airport; between Beltsville, Md. and Washington National Airport; and between Albany, Calif. and San Francisco Airport, etc.



## Testing Methods

All samples taken in the CCC operations were tested at regional laboratories of the Grain Division of the Agricultural Marketing Service, U. S. Dept. Agr. The following tests of bottom and balance samples were made according to the rules of the NCPA 3/ following the methods of the AOCS:

1. Moisture and volatile matter
2. Free fatty acids
3. Appearance
4. Flavor and odor
5. Refined color (in most cases)
6. Bleached color

Grade and quality according to the rules 3/ were also reported.

Most of the samples from the drums (8 to 11 from each drum) were examined and analyzed by "Laboratory A" by all tests under the NCPA rules, following methods of the AOCS as follows:

1. Moisture and volatile matter
2. Free fatty acids
3. Appearance
4. Flavor and odor
5. Refined color
6. Bleached color
7. Refining loss (crude oils)

Refined oils were also tested for peroxide value (AOCS Cd 8-53) and AOM fat stability. 4/

A second laboratory, designated as "Laboratory B," tested the remainder of the samples from each drum (2-4 samples) for all the above characteristics. These oils were also bleached and deodorized, and tested again for AOM fat stability, and a Schaal oven test 5/ was run.

A number of duplicate samples were also tested by both laboratories. These analyses provided the data needed to relate results at one laboratory to those at the other. The relationships among data from the two laboratories are shown in table 8 (appendix). The correlation factors of the table were

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3/ National Cottonseed Products Association, Memphis, Tenn.

4/ The active-oxygen method (AOM) for fat stability (AOCS Cd 12-57) was not published at the time of the initiation of the project and the methods used for this test varied from AOCS in that the end-point was determined organoleptically and by approximate "break" in the peroxide value. A specific end-point of 100 peroxide value (PV) was not used.

5/ Using a 100 ml. sample at 140° F. in a forced-draft oven and determining the point of rancidity organoleptically at 24-hour intervals.

used to report data from Laboratory Bin terms of Laboratory A in order to obtain the maximum number of observations of the various characteristics on the basis of a single laboratory.

### Conditions of Storage

Thirty-eight of the field tanks were cylindrical, varying in diameter from 10 to 80 feet and in height from 15 to 42 feet and ranging in capacity from 150,000 to 8 million pounds of oil. Four of these tanks were in a horizontal position. Four tanks were rectangular, with a capacity of about 180,000 pounds each.

Most of the tanks were filled to about 95 percent of capacity and only 6 were less than 80-percent filled. Nothing is recorded as to the source of the oils or the method of extraction. None of the oils were graded lower than summer yellow and about half of the oils were prime bleachable on entering storage. Very few were graded "off in flavor and odor" at any time during storage.

Oils in drums came from 12 different sources and were extracted by 5 different processes. On entering storage 9 of the 12 refined oils in drums were prime bleachable and the other 3 were summer yellow.

The 8 crude oils stored in drums were secured from different sources and were refined to supply 8 of the 12 refined oils used in the study. Three of these oils were refined at the mill and the other five at a pilot plant. Of the eight crude oils all were "prime" except one which was "basis prime." At the time of entering storage six of the crude oils refined to bleachable oil.

The experimental drum project was initiated in June 1955, with 12 drums each of 2 different lots of refined oil (2 of the 12 sources for the refined oils noted above). Although these two oils were from different sources, they had been extracted by similar processes and had similar initial characteristics. Each lot was solvent-extracted and refined in miscella. This part of the project was set up to determine any differences in change of quality due to different storage conditions. Four drums (2 from each of the 2 lots of 12) were designated as "controls." Two were stored at Beltsville and two at New Orleans.

The control drums were set up to simulate the most general conditions of field-tank storage; namely, painted with aluminum, provided with breathers, and exposed to outside atmospheric conditions. Variations from these controls for the other 20 drums were as follows:

1. Two drums from each of the two lots were held at room temperatures, with duplicates at Beltsville and New Orleans.
2. One drum from each lot was painted black instead of aluminum.
3. One drum from each lot had no breather and was opened only at the time of sampling.
4. One drum from each lot was only half-filled.

5. One drum from each lot was half-filled and contained 2 ounces of iron filings.
6. One drum from each lot contained 4 pounds of added water.
7. One drum contained 2 ounces of iron filings.
8. One drum contained a food liner.
9. One drum was fogged with mineral oil prior to filling.
10. One drum contained 2 pounds of citric acid.
11. The oil in one drum was thoroughly agitated before sampling.
12. One drum was sealed after initial sampling and not opened again for sampling until after 2 years in storage, and then again after 3 years and 4 years in storage.

Eight of the other 10 lots of refined oil in drums were stored in duplicate. Six drums of one lot were stored at three locations (two at each location) and six drums of one lot were used for special tests of the effect of sun and rain. All of these lots of oils were placed in storage in the winter of 1956-57. Except for the six drums used to compare the effects of sun and rain, all of these drums were stored under control conditions. In February 1958, at the time of placing a field tank under observation for temperature recordings, one drum of the same oil as that in the tank was fully exposed to the atmosphere (control) and one drum was shaded and protected in a manner similar to the 2-million-pound-capacity field tank under observation.

All of the eight lots of crude oil in drums (from different sources) were controls and each lot consisted of two drums. Final samples were taken from all the drums (refined and crude) in the summer of 1959.

### Recording Data

The accumulated time-temperature units for the period of storage at the time of each sampling were recorded with the analyses of all the tanks and drums for the following characteristics of each sample:

1. Moisture and volatile matter
2. Free fatty acids
3. Refined color
4. Bleached color
5. Peroxide value (refined oils)
6. AOM fat stability (refined oils)
7. Refining loss (crude oils)

### CHANGES IN CHARACTERISTICS DURING STORAGE

In order to establish the relationships between the time-temperature factor and each quality characteristic, statistical correlations were made of the accumulated time-temperature units and the characteristics of the oils (as recorded above) at the time of sampling of each of the drums and of both the bottom and balance samples of each tank. The differences between the rate of change of any of the characteristics of the balance and bottom samples of oil in the same tank were rarely significant. Regardless of location of



storage, there were no significant differences among the rates of change of the characteristics of oils from similar sources stored in drums under the same conditions. Similarly, many of the different storage conditions did not cause differences in rate of change of characteristics in oils from the same source. Accordingly, for purposes of more practical analysis of the data, many of the individual correlations were grouped together. Correlation data for each of the drums and the balance and bottom samples of the tanks are not shown in the report.

### Moisture and Volatile Matter

Differences between the rates of change in moisture and volatile matter in the oils stored in drums were not significant.

Except in nine tanks, where free water was present in the bottom sample, the rates of change of balance and bottom samples of oil from the same field tank were not significant. Four of these nine tanks were horizontal and cylindrical, and free water was present in the initial bottom samples, indicating that water was present (after cleaning the tanks) before filling with oil. One of the nine tanks did not show the presence of free water until near the end of storage, whereas free water was present in the remainder of the tanks at various times during storage. Four of the 42 tanks showed free water in both the balance and bottom samples.

Bottom samples of 13 refined oils in drums (under various storage conditions) that were examined at the end of storage contained no free water, except the drum to which 4 pounds of water was added at the beginning of storage. The bottom portion of oil in this drum contained the original 4 pounds of water.

Moisture contents of some oils increased and others decreased during storage. Initial moisture content and the rate of change of moisture content were related. Moisture contents of oils that were high initially decreased, and those that were low initially increased, during storage. This relationship between the initial moisture and rate of change in moisture was highly significant. There were no significant differences in rates of change of moisture contents between crude and refined oils stored in drums, or refined oil in field tanks of up to 8 million pounds' capacity. Oils of varying initial moisture content are shown in figure 1, with relation to change during storage.

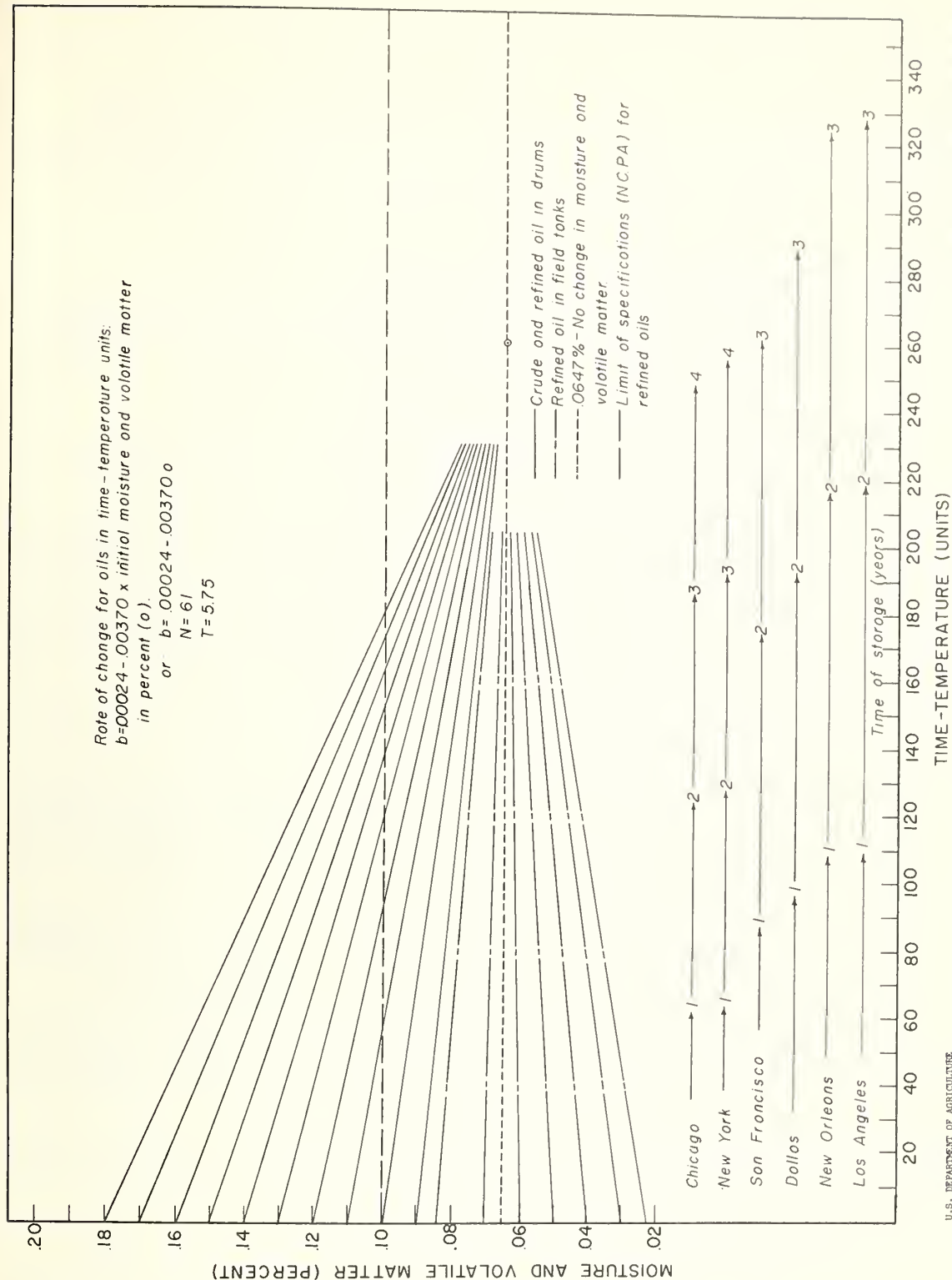
The rate of change, based on 61 observations of refined and crude oils, can be estimated from the formula:

$$b = .00024 - .00370a \quad (\text{Formula 1})$$

where  $b$  = the rate of change in percent for every time-temperature unit and  $a$  = the percent of initial moisture content (the "T" value is 5.75). <sup>6/</sup> By

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<sup>6/</sup> The "T" value is a measure of the significance of the correlation and equals the regression coefficient "b" divided by the standard error of estimate of "b". The higher the value, the greater the significance.



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FIG. 143-61(12) AGRICULTURAL MECHANICS: FERTILIZER

Figure 1.--Changes in moisture and volatile matter of stored cottonseed oils--related to time-temperature factor--stored at six locations.

substituting values of "b" for various values of "a" in the linear regression formula  $Y = a + bX$ , where Y = time-temperature units and X = percent of moisture content, the regression lines shown in figure 1 correspond to the formula:

$$Y = a + (.00024 - .0037a)X \quad (\text{Formula 2})$$

Although figure 1 7/ shows oils in drums only as having high initial moisture contents and refined oils in tanks only as having low initial moisture, the relationship between the initial moisture and rate of change is significant regardless of whether stored in drums or tanks, or as crude or refined.

The two important points illustrated in figure 1 are:

1. Refined oils that exceed the specifications for moisture content initially will, after various periods of storage, meet the specifications.
2. Moisture contents of oils that vary initially will approach a constant after about 2 to 4 years' storage, the time depending upon the conditions of storage.

This constant moisture content of 0.0647 percent may be the maximum solubility of water in stored crude and refined oils and apparently the temperature at the time of taking or testing the sample is not relevant. This solubility is somewhat lower than the constant for the solubility of water in cottonseed oil as shown by Parsons and Holmberg 8/ of 0.074 percent at 32° F. They also reported solubilities as high as 0.138 percent at 90° F.

#### Free Fatty Acids

The rates of change in free fatty acids were not significantly different between bottom and balance samples of oil from each tank (except as noted below) or between samples of oils in drums, except for differences associated with the sources of the oils.

The influence of free water, high water content, or both, in the oil was noted in several of the tanks. Free fatty acids showed highly variable changes in the bottoms of tanks of high-moisture oils during storage. In these cases only the characteristics of the samples of the balances were used for correlations. (In one case, representative samples could not be obtained in either the bottom or balance of the tank due to extreme variations in water.)

There were no significant differences between the rates of change of free fatty acids of refined oils in drums and of refined oils in field tanks.

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7/ Six areas are shown in time-temperature relationships which were interpolated from table 1.

8/ L. B. Parsons and C. O. Holmberg. Oil and Soap 14, 239 (1937)



However, all crude oils contained considerably more free fatty acids initially than any of the refined oils.

Free fatty acids in both crude and refined oils increased during storage, except when initial free fatty acids were around 0.05 percent for refined oils and around 0.62 percent for crude oils.

The rate of change, based on 42 observations of refined oils with initial free fatty acids under 0.05 percent, can be estimated from the formula:

$$b = .00050 - .01005a \quad (\text{Formula 3})$$

where  $b$  = the rate of change in percent for every time-temperature unit and  $a$  = the percent of initial free fatty acids (the "T" value is 5.13). For oils having initial free fatty acids over 0.05 percent, the rate of change can be estimated by:

$$b = .00619a - .00031 \quad (\text{Formula 4})$$

(The "T" value is 5.95).

The rate of change for crude oils having initial free fatty acids over 0.62 percent is estimated by:

$$b = .00523a - .00326 \quad (\text{Formula 5})$$

(The "T" value is 15.38).

However, increase of free fatty acids to 0.125 percent in refined oils (the limit of specifications for choice summer yellow oil) would require extremely long storage. Also, an increase to 3.25-percent free fatty acids in crude oils (at which percent crude oils are discounted as "off in flavor and odor") would require extremely long periods unless the initial percentage of free fatty acids was unusually high.

In order to determine the time-temperature units necessary for refined oils to increase to 0.125-percent free fatty acids, values of " $b$ " are determined from values of " $a$ " (under 0.125 percent), according to formula 4 and substituted in the formula  $Y = a + bX$ , which becomes:

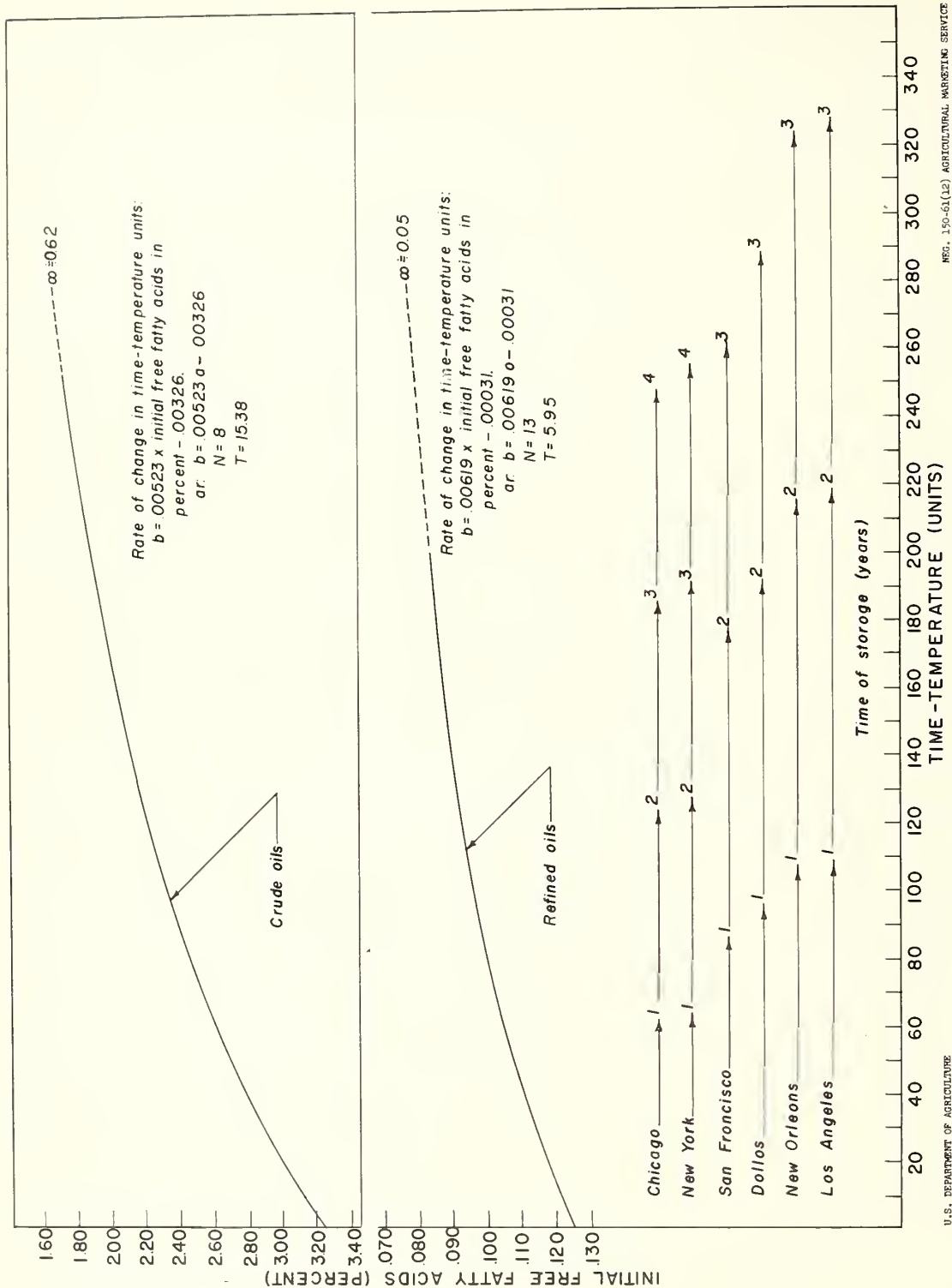
$$Y = a + (.00619a - .00031) X \quad (\text{Formula 6})$$

For example; if  $a = 0.110$ , then 40 time-temperature units are required for the oil to reach 0.125-percent free fatty acids (fig. 2).

Similar calculations are made to determine points on the "Crude oils" curve shown in figure 2, from the formula:

$$Y = a + (.00523a - .00326) X \quad (\text{Formula 7})$$

by substituting values of " $a$ " (under 3.25 percent) in formula 5.



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REG. 150-61(12) AGRICULTURAL MARKETING SERVICE

Figure 2.--Increases of free fatty acids in stored crude and refined cottonseed oils--increases to 3.25 percent in crude oils and to 0.125 percent in refined oils--related to time-temperature factor--stored at six locations.

Figure 2 also shows that infinite storage time would be required for refined oils of 0.05 percent initial free fatty acids to reach 0.125 percent and for crude oils of 0.62 percent initial free fatty acids to reach 3.25 percent.

### Refined Color--Refined Oils

Color of all the refined oils in the tanks and drums decreased during storage. There were no significant differences in the rates of decrease of color between the balance and bottom samples of oil in the same tanks. There also were no differences between duplicate and replicate samples of oil from drums from the same source, stored under the same conditions.

### Effect of Type of Storage Conditions

There were some differences in rates of color decrease between the controls (drums painted aluminum, with breathers, and stored outside) of the same oils when the drums were stored inside, without breathers or half-filled, as shown in table 9, appendix. Table 9 (appendix) also includes data of the drum which was opened only four times during a 4-year storage period.

### Relation Between Initial Color and Rate of Decrease

The rates of color decrease of all refined oils in tanks and drums were significantly related to the initial color. The formula for estimating color decrease, calculated from correlations of oils in 42 field tanks and in 12 drums is as follows:

$$b' = .00283 - .00157a \quad (\text{Formula 8})$$

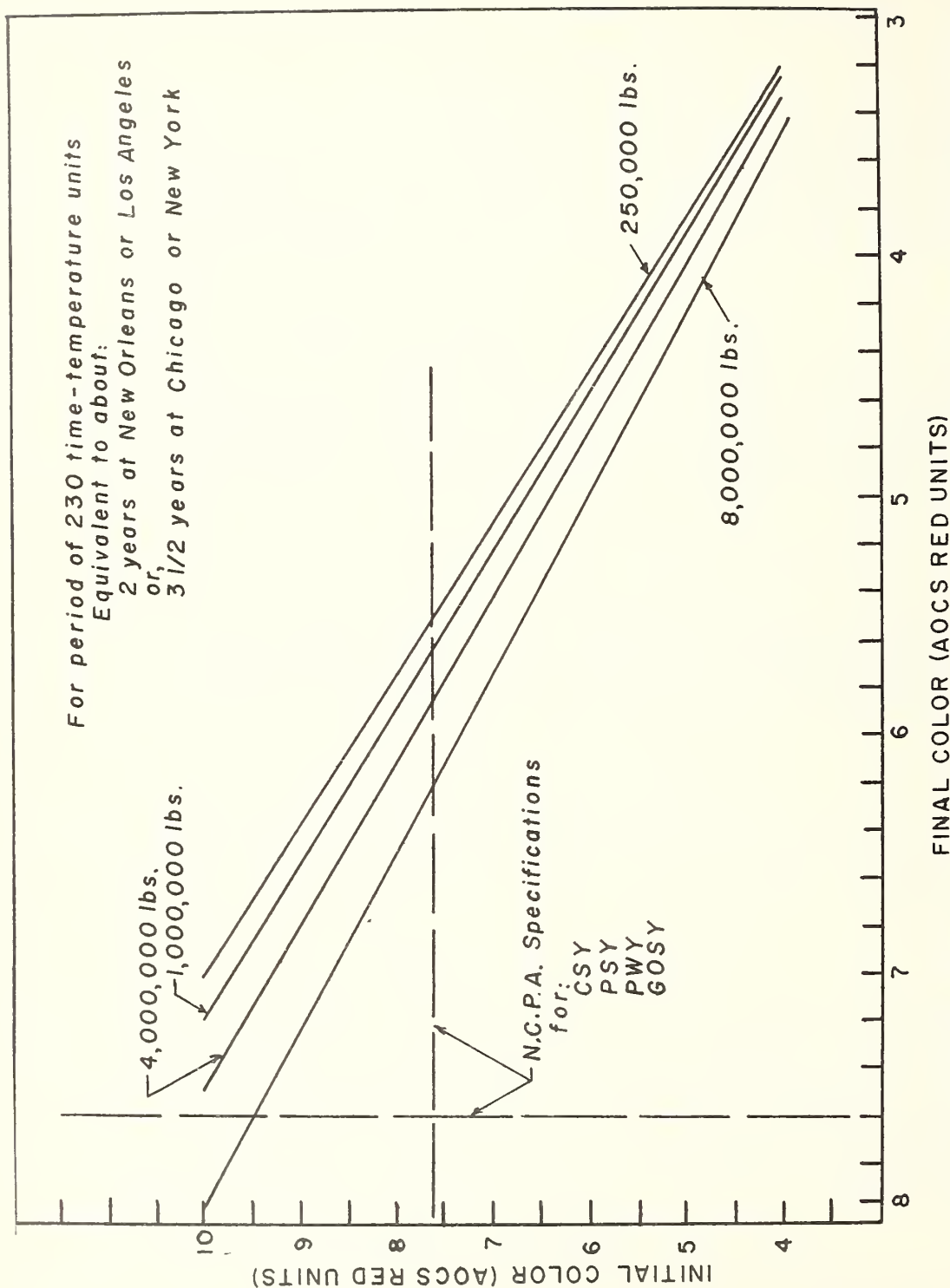
where  $b'$  = the rate of color decrease per time-temperature unit and  $a$  = the initial color as determined from original correlations of each lot of oil (the "T" value is 5.41).

### Effect of Quantity of Oil

When the vertical cylindrical tanks, filled to 80 percent or more of capacity, were grouped statistically and the rate of color decrease ( $b'$ ), for each tank of oil, was determined by formula 8, the quantity of oil affected the rate of color decrease. The color of larger volumes of oil decreased at a slower rate than the color of smaller volumes of oil. The ratio of the calculated  $b'$  (by formula 8) and the  $b$  (determined by the individual correlations) provides a factor,  $f$ , for the quantity of oil in these tanks, as follows:

$$f = 1.02 - .00449 (b/b') \quad (\text{Formula 9})$$

where  $f$  is the factor for every 100,000 pounds of oil in the filled vertical cylindrical tanks. The use of this factor is shown in figure 3 where the



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Figure 3.--Relations of initial and final colors of stored refined cottonseed oils--stored in field tanks filled to capacity.

relationships between initial and final colors of four tanks of oil for 230 time-temperature units are illustrated. (See table 1 for the time of storage at several locations for corresponding time-temperature units.)

The formula for the relationships in figure 3 is:

$$Y = a + (.00283 - .00157a)fX \quad (\text{Formula 10})$$

where  $f = 1.009$  for 250,000 pounds,  $0.975$  for 1 million pounds,  $0.840$  for 4 million pounds, and  $0.661$  for 8 million pounds of oil in the tanks. Also,  $Y$  = the final color in red units,  $a$  = the initial red color and  $X = 230$  (time-temperature units). (Formula 10 can be recognized as the usual regression formula  $Y = a + bX$ , with substitution for formulas 8 and 9.)

Figure 3 shows that in oils of low initial color, there was little difference in the final colors in tanks varying in quantity from 1/4 to 8 million pounds, whereas in oils with high initial color, the color of oils in the smaller tanks decreased at a higher rate than the color of oils in the larger tanks.

Figure 3 also notes the limit of specifications (rules of the NCPA) for: choice summer yellow (CSY), prime summer yellow (PSY), prime winter yellow (PWY), and good off summer yellow (GOSY) oils, at a color of 7.6. Some oils can be upgraded according to the rules by decreasing in color during storage. In other words, summer yellow oil can be upgraded to choice summer yellow. This is shown in figure 4, on the basis of the period of storage necessary for four tanks of oil of varying initial colors above 7.6 to decrease in color to 7.6.

Points on the four curves shown in figure 4 are determined from formula 10 by using various initial red colors greater than 7.6; as an example, it requires 100 time-temperature units for a volume of oil (initial red color of 8.7) in the amount of 250,000 pounds in a filled vertical cylindrical tank to reduce in color to 7.6.

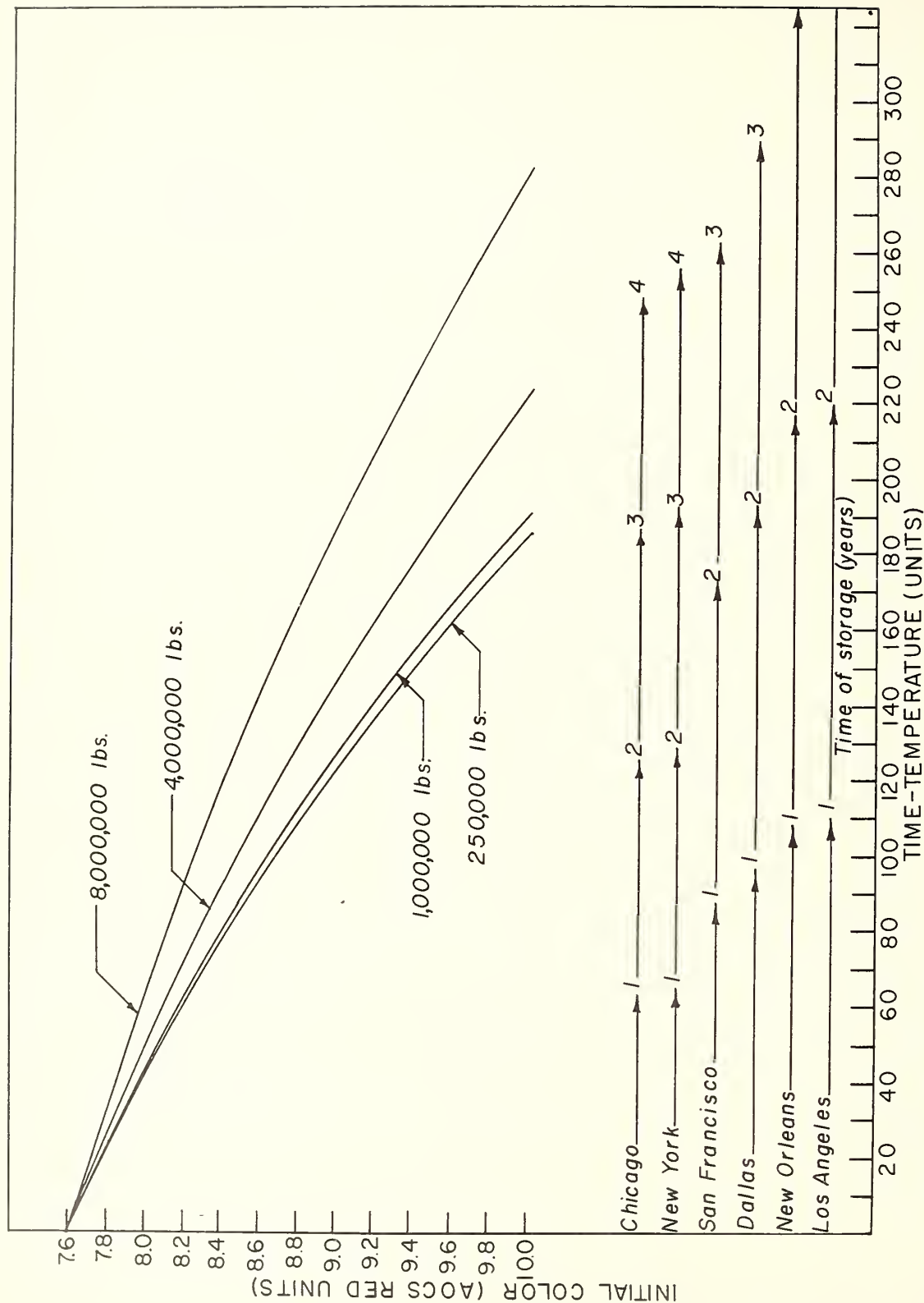
Only one grade of refined oil is designated in market quotations, namely, prime bleachable summer yellow (PBSY). (PBSY oils have a maximum limitation of 2.5 on bleached color; however, oils lower than 2.5 bleached color generally have a refined color of 7.6 or lower.) Opinions from various buyers in the industry indicate that, when oils below the PBSY grade are traded, CSY and PSY oils are discounted substantially and SY oils are discounted even further --as much as 100 points, or 1 cent per pound.

Other factors enter the trading of oils below the grade of PBSY. An important factor is the peroxide value (PV) of the oil, although this test is not a requirement of the NCPA rules. The increase in PV with storage is discussed later.

#### Effect of Air Space in Tanks

There were six vertical cylindrical tanks, which were filled to less than 80 percent of capacity. The effect of greater air space in proportion to the





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Figure 4.--Decreases in color to 7.6 red of stored refined cottonseed oils--related to time-temperature factor--in field tanks filled to capacity at six locations.



quantity of oil in these tanks is shown in table 10 (appendix) by comparison with tanks containing equivalent quantities of oil when filled to capacity. There are some indications that the color of oils in the partially filled tanks decreased at a faster rate than it would have in filled tanks. This effect is more apparent in oils stored in drums, where the color of oils in the half-filled drums decreased at the rate of 1.33 as compared to the rate of oils in the control drums (table 9, appendix).

### Effect of Surface Area of Oil

Four cylindrical tanks were horizontal. The effect of greater surface area of the oil can be shown by comparing the rates of color decrease of oil in these tanks with the rates of color decrease of the same quantity of oil stored in a vertical cylindrical tank (table 11, appendix). While these four tanks were filled to about the same percentage of capacity as the oils in the filled vertical cylindrical tanks, the color of the oils was estimated to decrease 16 percent faster. The surface area of the oil in the horizontal tanks (95-percent filled) was 182 square feet, whereas the surface area of the same quantity of oil in a vertical tank would have less than one-half this surface area, or 82 square feet.

The effect of even greater surface area of the oil can be shown by comparing oils in rectangular tanks with oils in the vertical cylindrical and in the horizontal cylindrical tanks (table 12, appendix). Three of the rectangular tanks were filled to about the same percentage of capacity with about the same quantity of oil and the color of oils in these tanks decreased about 24 percent faster than the color of oils in the vertical cylindrical tanks.

The surface area of the oil in the larger rectangular tanks was 4,915 square feet compared with 314 square feet in the larger vertical cylindrical tanks. The surface area of the oil in the rectangular tanks is over 15 times the area of the same quantity of oil in the vertical cylindrical tanks, and the surface area of the horizontal cylindrical tanks is twice the area of the same amount of oil in the vertical cylindrical tanks. These differences could account for the greater color decrease of oils in rectangular tanks as compared with the color decrease in vertical and in horizontal cylindrical tanks.

### Refined Color--Crude Oils

#### Comparison of Color Change

The color of all the crude oils stored in drums, except the oil extracted by the filtration process, increased during storage.

There were no significant differences in rates of color change between duplicate or replicate drums of oil from the same source. There also were no significant differences among the three oils from different sources extracted by expeller or any differences between the oils from the two sources extracted by prepress solvent. Accordingly, the oils from these two latter extraction

methods were grouped. Figure 5 shows the color change for the five different extraction methods over periods of storage based on an original color of 6.00 (the initial color of the eight oils in the project average 6.03). As "a" in the regression lines shown in figure 5 is 6.00 in all cases, the differences in the formulas are determined by the value of "b" in each case, from the formula  $Y = a + bX$ .

Although the number of crude oils in the project was limited, the rates of color change among the five extraction processes varied slightly within each process but differences among processes were highly significant. The small color decrease of the oil extracted by the filtration process is quite important in the consideration of oils from storage when compared with oils extracted by other methods. Change of grade from "prime" down to "basis-prime" and even "off-crude" occurred in oils extracted by other processes during rather short storage. The behavior of the filtration-extraction process crude oil (as concerns color change) resembles the behavior of oils that were stored as refined and not as crude.

#### Comparison of Cup and Plant Refining

In order to have refined oils which were made from specified crude oils, part of each lot of all the crude oils were refined. Three of the crude oils were refined at the mills and five were refined at a pilot-size refinery.

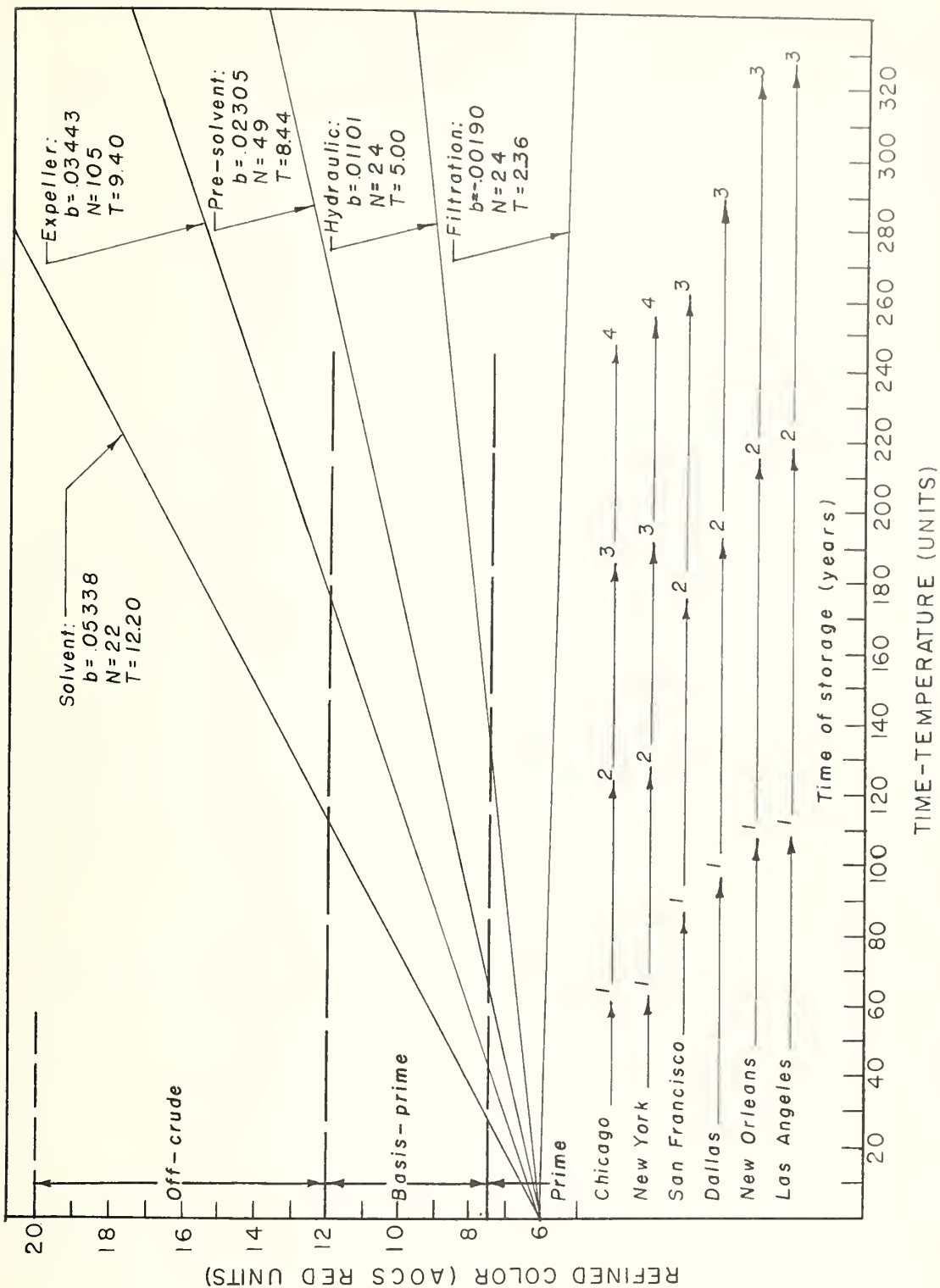
A comparison of the refined color after cup (laboratory) refining of the crude oil compared to the refined color after plant refining is shown in table 2.

Table 2.--Comparison of initial refined colors by cup and plant refining 1/

Location of oil storage	Refined color <u>2/</u>		
	Cup	Plant	Difference
Alabama	7.41534	7.27502	- 0.14032
Texas	5.42949	5.35825	- .07124
California	6.38355	8.20189	+ 1.81834
		Average	+ 1.60678
	Cup	Pilot plant	Difference
Arkansas	6.30646	7.90479	+ 1.59833
Tennessee	5.53307	4.59429	- .93878
Arkansas	6.35830	6.90617	+ .54787
Mississippi	5.81063	5.83749	+ .02686
Mississippi	4.97272	5.71862	+ .74590
		Average	+ 1.98018

1/ Initial refined colors determined by correlation.

2/ In red units according to methods of AOCS.



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Figure 5.--Changes in refined color of stored crude cottonseed oils--extracted by different methods--related to time-temperature factor--stored in drums at six locations.

Both refined and bleached colors were reported on only 34 of the CCC field tanks of oil. The bleached color of two of these oils was reported as "off-brown" and these oils were not used in the individual correlations.

There were no significant differences in the rates of change in bleached color among the bottom and balance samples from the same tanks. There also were no differences among duplicate and replicate drums of oil from the same source.

The bleached color of the oil in 20 of the 34 tanks decreased, whereas the color of the remainder increased during storage. The bleached color of all but one of the refined oils in drums increased during storage.

#### Relation of Initial Refined and Bleached Colors

Figure 6 shows the relationship among the initial refined and bleached colors of 52 oils in the project. This includes all of the tanks of refined oils and the drums of both crude and refined oils. The curve of Bailey <sup>9/</sup> is also shown. A refined color of 7.6 on the Bailey curve corresponds to a bleached color of 2.39, somewhat under the 2.5 specified for PBSY oils. This better bleachability of the oils in Bailey's work could be accounted for in that more hydraulic than expeller or solvent oils were produced at that time.

#### Relation to Change of Bleached Color

If formula 11 ( $BC = .39108 RC - .28048$ ), shown in figure 6, is used to calculate an initial bleached color from the refined color for each of the 52 oils in the project, the differences among these calculated bleached colors and the initial bleached colors as determined in the individual correlations of each oil show a relationship between the bleached color of the oils and the rate of color change during storage. This formula can be given as:

$$b' = -.00188 (a - a') \quad (\text{Formula 12})$$

where  $b'$  is the rate of change of bleached color for each time-temperature unit,  $a$  is the correlated initial bleached color, and  $a'$  is the bleached color calculated by formula 11 shown in figure 6. (The "T" value = 3.55).

The regression formula for change in bleached color can then be given as:

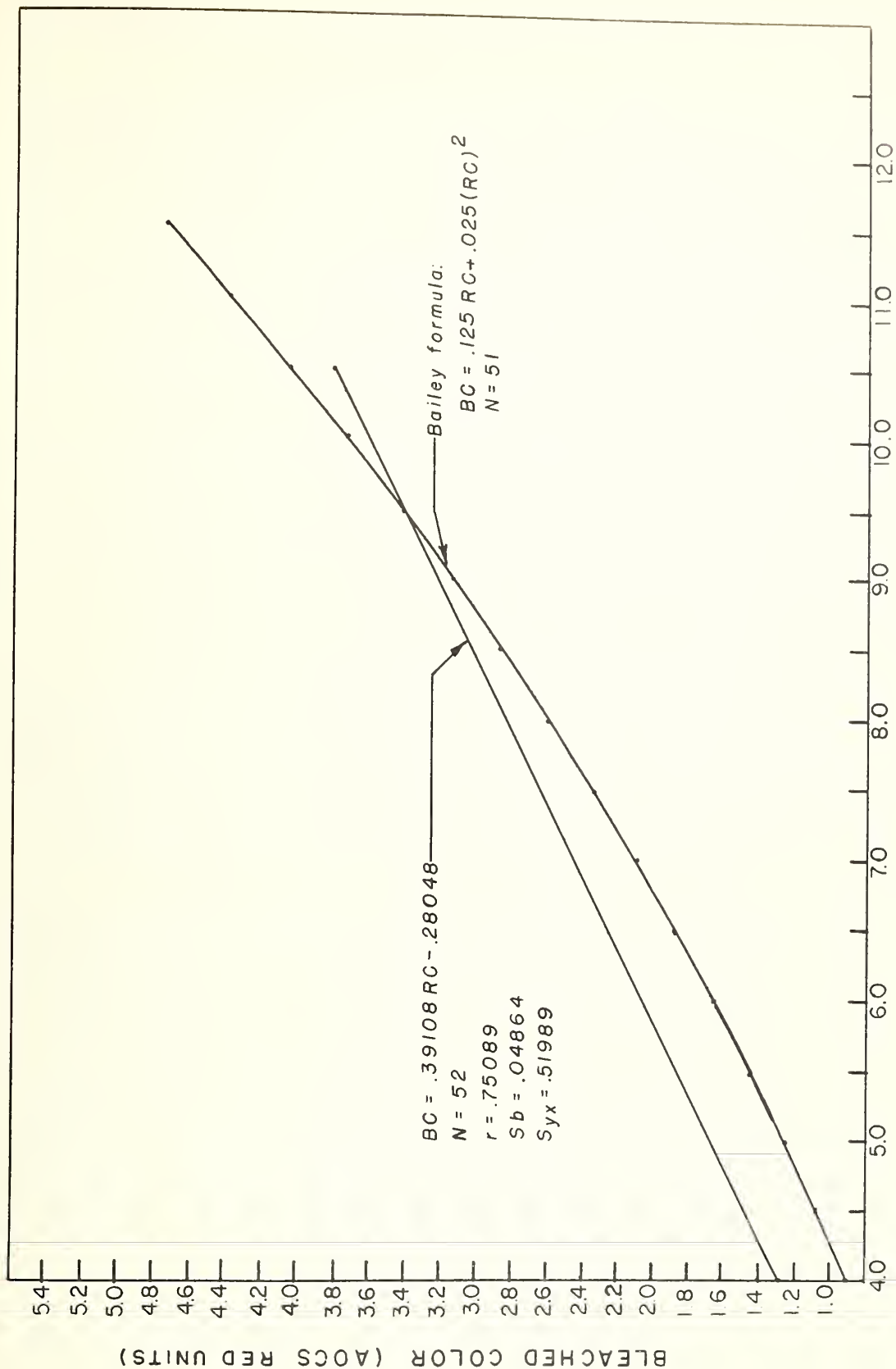
$$Y = a + \sqrt{-.00188 (a - a')} X \quad (\text{Formula 13})$$

It is obvious from this formula that if the initial and calculated bleached colors are the same ( $a$  and  $a'$ ), there will be no change in bleached color

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<sup>9/</sup> A. E. Bailey. Cottonseed and Cottonseed Products. Interscience Publishers, Inc., New York, 1948.





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 Figure 6.--Relations of initial refined and bleached colors of crude cottonseed oils.

during storage. If the calculated color ( $a'$ ) is greater than the initial ( $a$ ), there will be an increase in color during storage and if the reverse is true, a decrease in color.

Figure 7 applies this formula to seven oils having different initial refined colors but having the same initial bleached color of 2.5 (limit of specifications for bleachable oil). Oils of 2.5 initial bleached color will increase in bleached color during storage if initial refined color is above 7.1 and decrease if it is below 7.1.

Figure 8 shows that by specifying time-temperature units, relationships can be shown among initial and final bleached colors of oils having different initial bleached colors and having initial refined colors of 4, 5, 6, 7, 8, 9 and 10. (Formulas 11 and 13 provide the data needed for plotting lines in figure 8.) The limit of specifications for bleachable oil is also shown in the figure.

It is important to estimate the effect of storage on those oils which are not bleachable initially but become bleachable. These oils would have initial refined colors below 7.1 (fig. 9). Figure 9 shows oils having different initial bleached colors above 2.5 and having initial refined colors of 4, 5, 6, and 7. (Oils of 2.5 initial bleached colors and initial refined colors over 7.1, increase in bleached color during storage.)

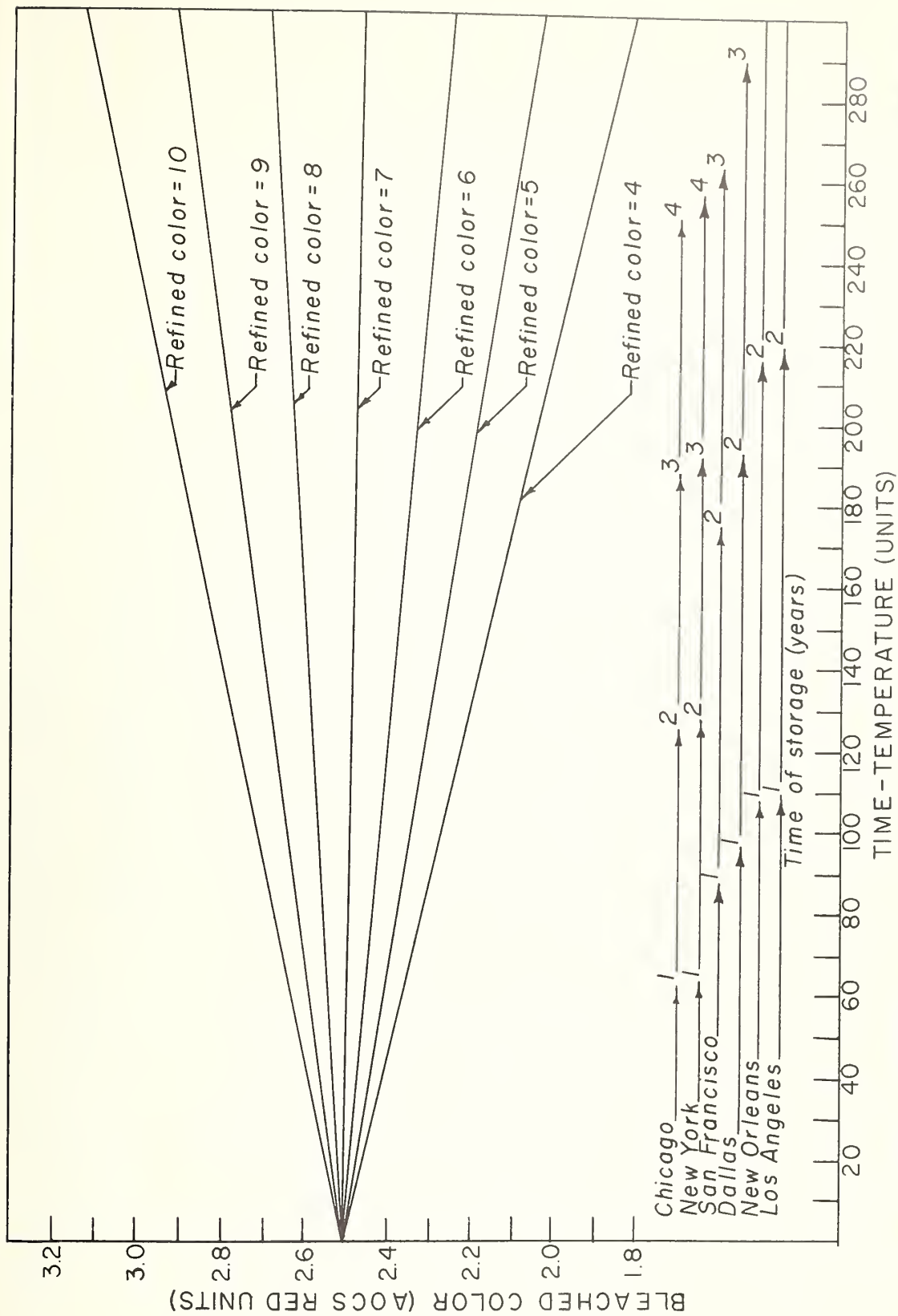
#### Bleached Color--Crude Oils

All of the crude oils stored in drums increased in bleached color during storage. The rates of increase in bleached color of the oils extracted by the five different methods were significantly different from each other (fig. 10). The increase in bleached color follows the same pattern as was indicated in figure 5 where an increase in refined color is shown; however, the rate of color increase is not as great for the bleached colors as for the refined colors.

An initial bleached color of 2.066 was used in figure 10 for each of the oils (average for all the oils is 2.074), which is the bleached color as calculated by formula 11 for a refined color of 6.0. By comparing refined and bleached colors at various storage periods found in figures 5 and 10, ratios of bleached to refined color can be related to storage periods (fig. 11).

The initial ratio of 2.066 to 6.0 (0.344) for bleached to refined color shows that, during storage of the five oils processed by different methods of extraction, bleached color increased with relation to the refined color. This increase is quite similar for four of the methods. The solvent-extracted oil, on the other hand, increased in bleached color at a far greater rate than the other four methods. In other words, during storage, solvent-extracted oil stored as crude became increasingly more difficult to bleach than oils extracted by the other four methods.

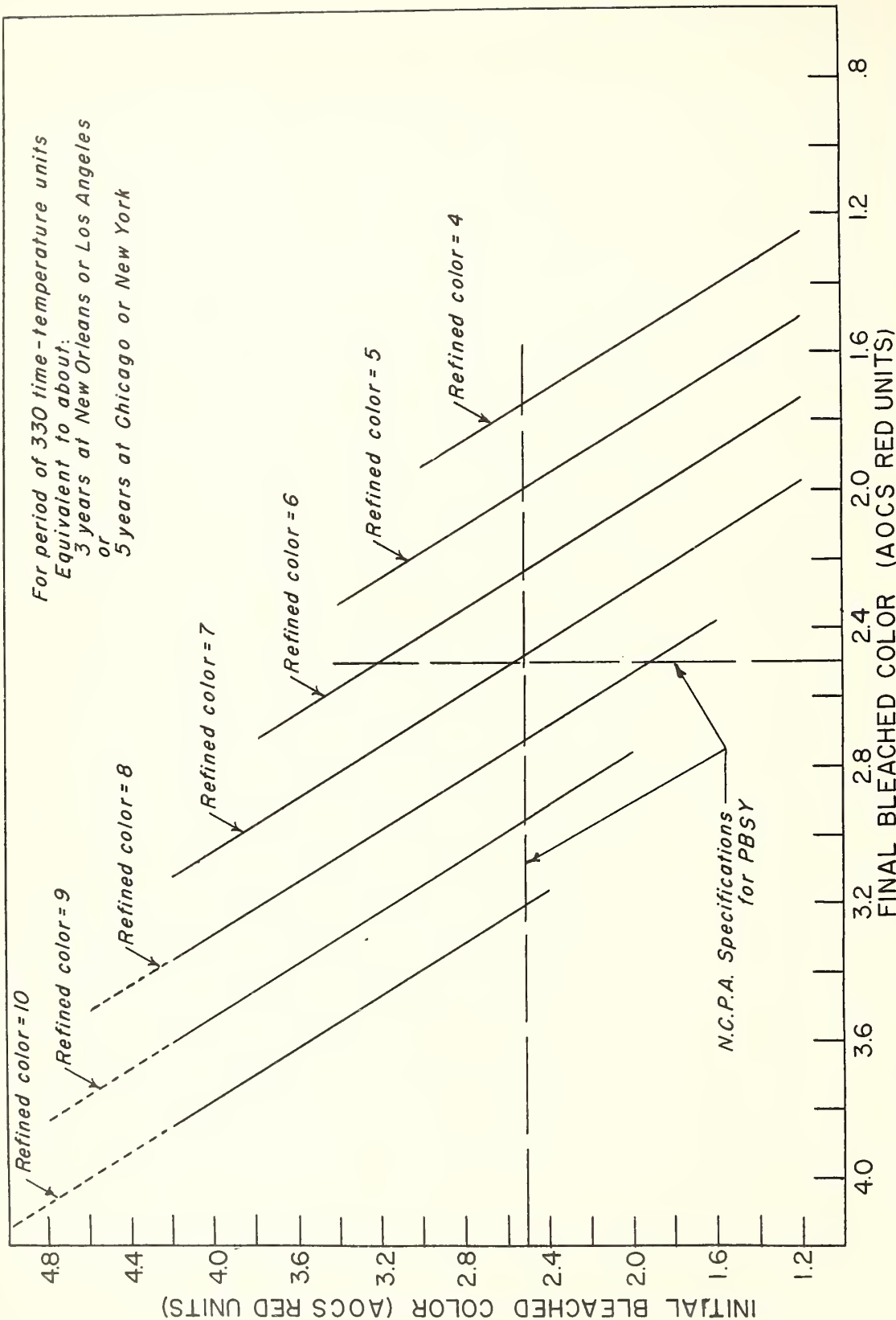




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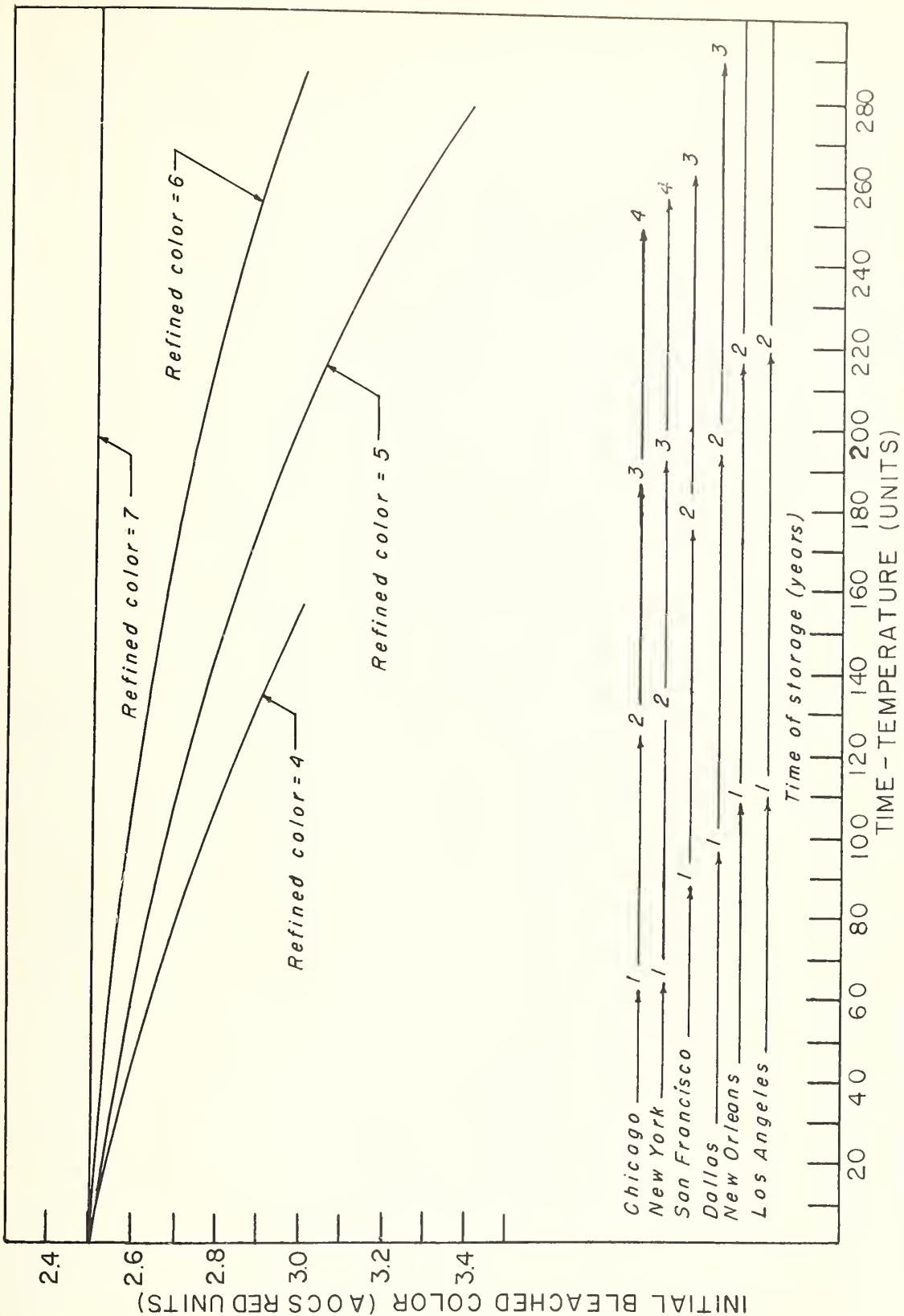
Figure 7.--Changes in bleached colors of seven stored refined cottonseed oils--related to time-temperature factor--initial red colors of 4 through 10--stored at six locations.



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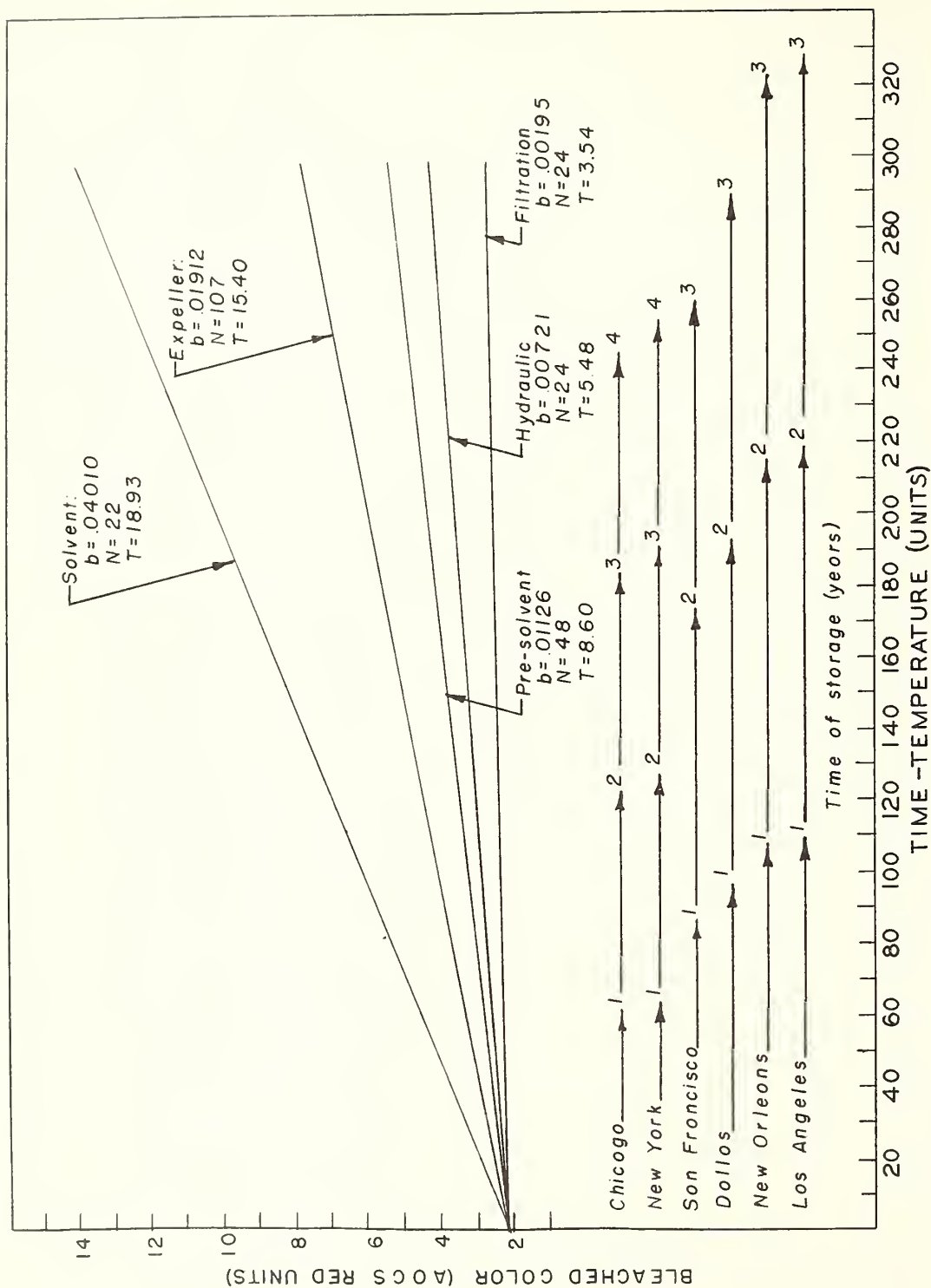
Figure 8.--Relations of initial and final bleached colors of stored refined cottonseed oils---initial refined red colors 4 through 10.



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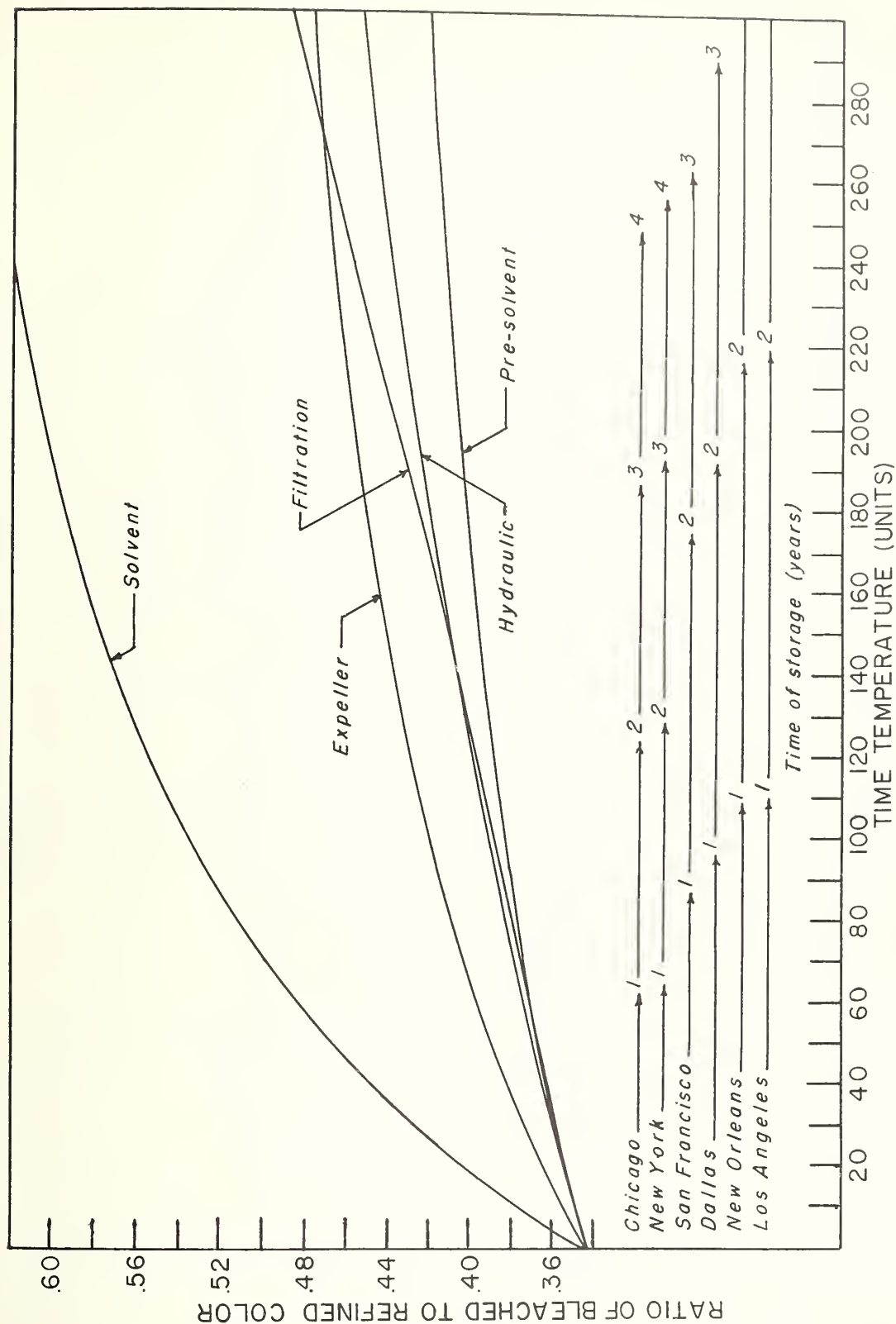
Figure 9.--Decreases in bleached color to 2.5 red of four stored refined cottonseed oils--initial refined red colors of 4, 5, 6 and 7--related to time-temperature--stored at six locations.



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Figure 10.--Increases in bleached color of stored crude cottonseed oils--extracted by different methods--related to time-temperature factor--stored in drums at six locations.



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Figure 11.--Ratios of bleached to refined colors of stored crude cottonseed oils--extracted by different methods--initial refined colors are 6.0 red and initial bleached colors are 2.066 red--related to time-temperature factor--stored in drums at six locations.



If the initial refined and bleached colors and the extraction method for crude oil are known, its probable color after different storage times can be calculated by the use of formulas 11 and 13.

No crude oils were stored in field tanks in the project. Large field tanks of crude oil probably would not change color as fast as the oils in the drums. An estimate of this relationship is discussed later in the report.

### Peroxide Value

The peroxide value of all the refined oils in drums increased during storage. 10/ There were no significant differences in the rates of this increase among any of the oils stored under control conditions, or among most of the oils stored under other conditions. However, differences among rates of peroxide value increase were significant among oils in control drums, in half-filled drums, in drums stored at room temperatures, and in no-breather drums with and without exposure to the sun (table 13, appendix).

Nine of the tanks at Houston, Texas, were sampled after 1 year of storage and tested for peroxide value. The amount of refined oil in these tanks ranged from 170,000 to 317,000 pounds. Although there were few differences in peroxide values among these tanks of oil, the average peroxide value was less than that found in control drums after similar units of time-temperature. A 2-million-pound tank of refined oil (stored under experimental control at Bayonne, New Jersey) showed even lower peroxide value.

Data indicate that the presence of air, as well as time-temperature, is an important factor in the increase of peroxide value during storage of oil in drums (table 13, appendix).

Lack of a sufficient number of samples from the field tanks tested for peroxide value prevents reliable estimation of change in peroxide value of oils in different sizes of tanks. A comparison of changes of peroxide value during storage of oil in drums and field tanks is made later.

### AOM Fat Stability--Refined Oils

All of the refined oils in drums decreased in AOM fat stability during storage. 11/ Although the decrease in AOM was found to correspond to an increase in peroxide value, AOM fat stability was not as closely related to

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10/ The Trading Rules of the NCPA do not require a peroxide value test in the grading of cottonseed oils, nor does the Methods of the AOCS state that this test measures deterioration. The Methods states that ".....generally assumed to be peroxide or other similar products of fat oxidation."

11/ The AOM (active oxygen method) fat stability test is not required in grading oils according to the NCPA Trading Rules. Industry seldom uses this test as an indicator of quality of refined cottonseed oils. It is, however, often used on deodorized cottonseed oils (cont'd. - see footnotes on page 29)

storage conditions as the peroxide value test (table 14, appendix). There is, however, a high degree of relationship between the analyses from the two tests when applied to the stored refined oils.

### Relation of Peroxide Value and AOM Fat Stability

More than 500 samples of refined oils during storage were tested for both peroxide value and AOM fat stability in the project. Over 85 percent of these samples were tested at Laboratory A. Relationships between the peroxide value and AOM fat stability are shown in figure 12.

Figure 12 shows curves from 431 tests for PV and AOM on the refined oils and from 69 tests on the bleached and deodorized oils. The refined oil curve indicates an AOM of 0 equal to about 160 PV. The present AOCS tentative method for AOM was not used in the project. The end-point was determined organoleptically and by "break" (a much more rapid increase) in PV, instead of using 100 PV as the end-point. This indicates that the end-point of 100, according to the AOCS method, is too low for stored refined cottonseed oils.

An estimation to show more clearly the effects of bleaching and deodorizing on the AOM fat stability of the stored refined oils is made by combining the two curves in figure 12 (fig. 13).

Three points of most interest in figure 13 are:

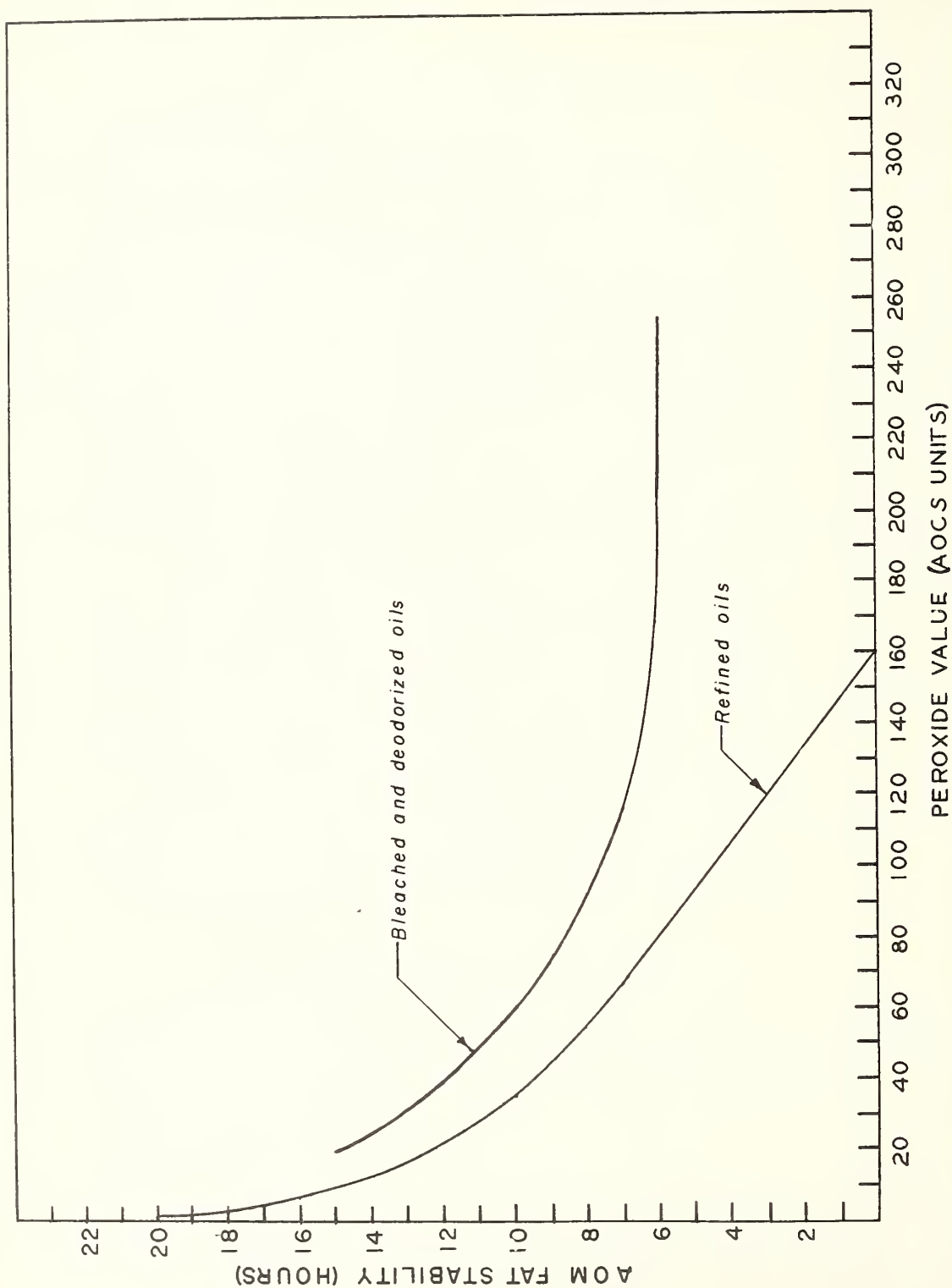
1. Zero AOM's of the refined oils are improved to about 6 hours by the processes of bleaching and deodorizing.
2. When the AOM value is below 14 hours, the refined oils are improved by bleaching and deodorizing; the lower the AOM value, the more the improvement.
3. When the AOM value is above 14 hours, refined oils show decreased AOM's after bleaching and deodorizing; the higher the original AOM, the more the decrease.

### The Schaal Oven Test

All refined oils which were bleached and deodorized were also subjected to the Schaal oven test. Correlations between the AOM fat stability after bleaching and deodorizing and the oil stability as determined by the Schaal oven test were statistically significant with a correlation coefficient of

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11/ (cont'd. from page 28) and end-products from cottonseed oils, such as shortenings. The Methods of AOCS state that ".....The length of this period of time (to reach zero hours AOM) is assumed to be an index of resistance to rancidity. The exact relationships between the peroxide value (at the end-point of the test) and such qualities as shelf life, actual rancidity, and oxidative stability have not been established."

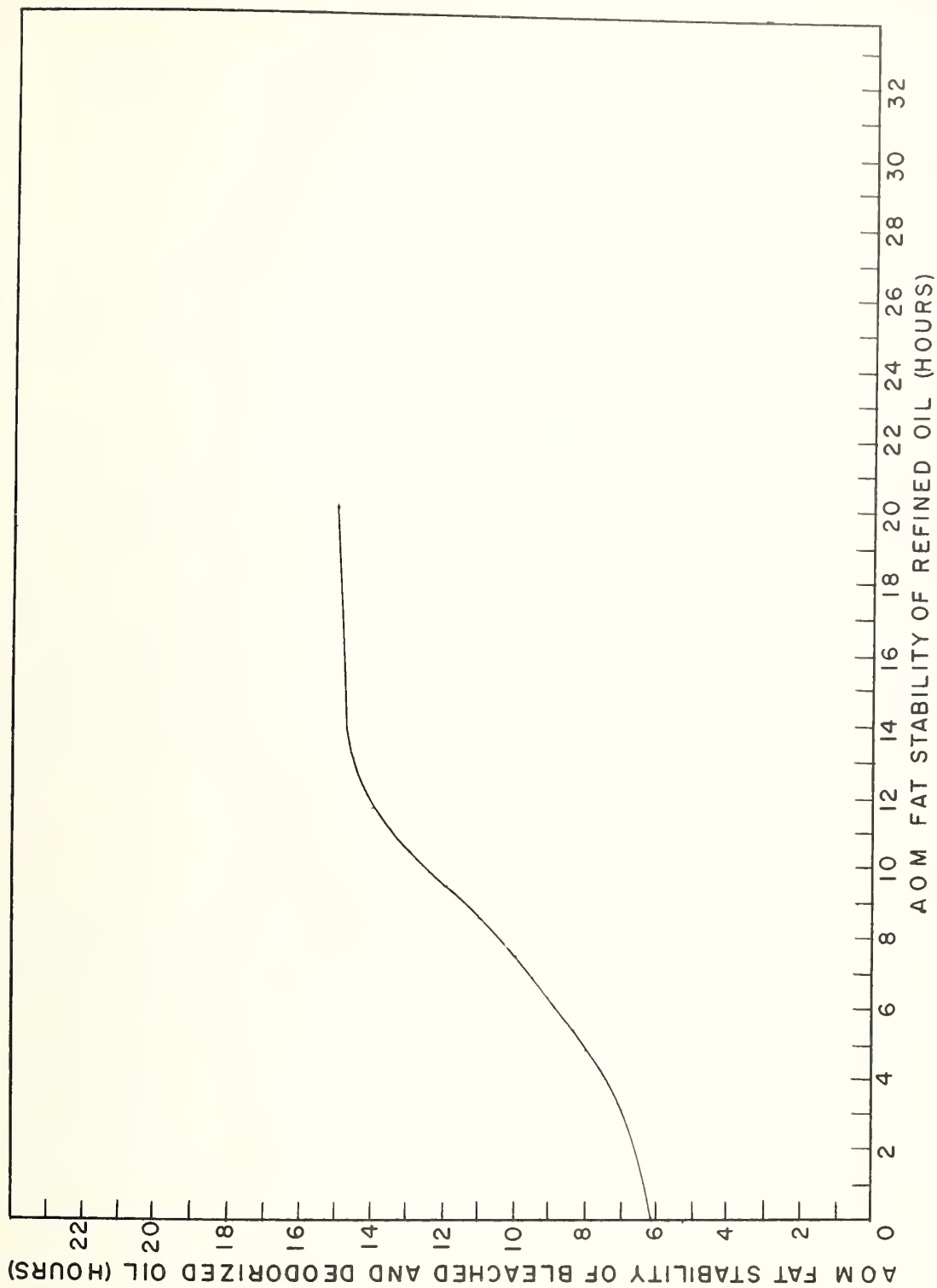


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PEROXIDE VALUE (AOCs UNITS)

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Figure 12.--Relation of peroxide value to AOM fat stability of stored refined cottonseed oils--before and after bleaching and deodorizing.



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Figure 13.--Relation of AOM fat stabilities of stored refined cottonseed oils--before and after bleaching and deodorizing.

.6078 for 59 samples. <sup>12/</sup> However, variations in the results of this test showed a standard error of estimate, in the correlation, of 54 hours. On this basis, the Schaal test is not as good a test as the AOM fat stability to differentiate among conditions of the stored oils.

Data in the present report show that, compared to the AOM fat stability and the Schaal oven tests, the peroxide value test is the best measure of change in "resistance to oxidation" (see footnotes 10 and 11, pp. 28-29).

### AOM Fat Stability--Crude Oils

The darker color of crude oils, as compared to color of refined oils, masks the color change at the end-point of the peroxide value test, hence AOM fat stability tests were not made on crude oils. AOM fat stabilities were run on some of these oils after refining and after the further processes of bleaching and deodorizing. This was done on 47 samples of crude oils after various storage up to over 200 time-temperature units.

There were no significant relationships between the period of storage and the AOM fat stability of the crude oils after refining, bleaching, and deodorizing. The average AOM was 13.53 hours, with a standard deviation of 2.41 hours, regardless of time in storage or source of the oil. (All of these crude oils were stored under control conditions; namely, in drums painted aluminum, with breathers, and stored outside.)

These same oils stored (under control conditions) in the refined, instead of the crude state, showed AOM fat stabilities varying from 13 to 15 hours before storage, indicating no apparent decrease during storage in the crude state. It may be assumed that there were no significant increases in peroxide values of the stored crude oils, in view of the relations between PV and AOM shown in figure 12.

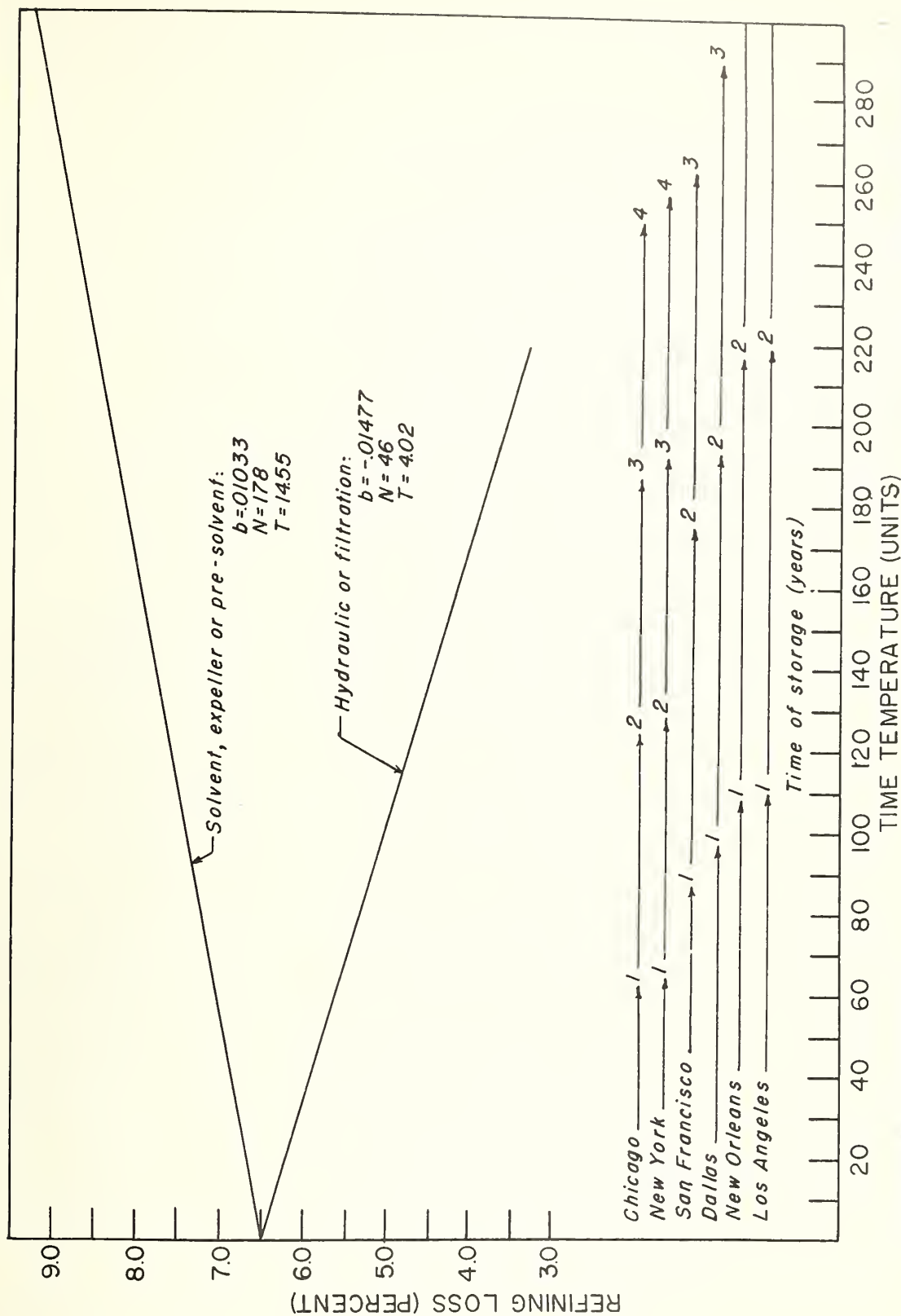
### Refining Loss

Significant changes in the refining loss of the crude oils during storage were found to be related to the method of extraction. There were no significant differences among the rates of change in the refining loss during storage of those oils extracted by the solvent, expeller, and prepress solvent methods. Refining losses of all oils extracted by these processes increased during storage. On the other hand, oil processed by the hydraulic- and filtration-extraction processes decreased in refining loss during storage with no meaningful differences among the rates of change. There were, however, significant differences in rates of change of refining loss between the two groups of oils. This is shown in figure 14 where the comparison is made with an initial refining loss of 6.5 percent (an average of the two groups based on correlation).

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<sup>12/</sup> Regression formula:  $Y = 359.85 + 5.89 X$ , where Y = Schaal test in hours and X = AOM in hours.





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Figure 14.--Changes in refining loss of stored crude cottonseed oils--extracted by different methods--related to time-temperature factor--stored in drums at six locations.

Refining loss is a factor in the settlement price for crude oils under the trading rules and the method of extraction, because of its effect on refining loss, may determine whether the value of crude oil increases or decreases during storage. This is discussed further under "Evaluation of Stored Oils."

### Relation of Storage in Drums and Tanks

The contents of moisture and volatile matter and of free fatty acids present in crude and refined oils have been shown to change at about the same rate during storage in drums and in field tanks (up to 8 million pounds' capacity); however, the rates of change of oils in refined color, peroxide value, AOM fat stability, and the Schaal oven test differed. Since results of the last two tests varied widely and are directly related to peroxide value which is a more reliable test, they will not be discussed further.

As there were no field tanks of crude oil in the project, it is desirable to make some estimates as to how the crude oils (stored in drums) would behave if they had been stored in field tanks. Lack of data prevents making a reliable estimate of the rate of change of the characteristics of crude oils stored in tanks. However, a comparison of the refined colors and peroxide values of refined oils stored in drums and tanks might indicate probable behavior of crude oil stored in tanks.

The best estimate that can be made of the rate of change of these two characteristics during storage, comparing drums and field tanks, is shown in table 3. Note that the ratios comparing the changes in color and peroxide values of oils in the two types of storage are almost identical.

In the industry, decrease of color is generally assumed to be an oxidizing reaction and the high relationship shown between peroxide value and color change bears this out. Other data in the project (not shown) also show this highly related agreement between increase in PV and decrease in color.

The relationships among the drums and tanks in table 3, which are calculated from changes in color and peroxide value, may or may not be valid for crude oils, due to the presence of gossypol, which is eliminated in the refining process. The method of extraction determines the amount and nature of the gossypol and related pigments in the crude oils (fig. 5). It is known in the industry that gossypol and gossypol-like pigments increase in intensity very rapidly in most crude oils in field tanks and that these changes are associated with strong antioxidant properties of the pigments. This was noted in the report where there were minor decreases in AOM fat stability, and little increase in peroxide value was indicated during the storage of crude oils in drums. Accordingly, no comparison can be made of crude and refined oils in drums, based on change in color and peroxide value, which could show rate of change of crude oils in field tanks as compared to crude oils in drums.

Table 3.--Summary of data used to estimate differences among changes in refined color and peroxide value during storage of refined cottonseed oils in drums and in field tanks

Container and amount of oil <u>1/</u>	Refined color <u>2/</u>		Peroxide value <u>4/</u>	
	Decrease in time-temperature <u>3/</u>	Ratio to decrease	Increase in time-temperature <u>5/</u>	Ratio to increase
	<u>Pounds</u>	<u>Per unit</u> <u>Drums</u>	<u>Per unit</u> <u>Drums</u>	
Drum:				
420	.00502	1.00	.37314	1.00
Tanks:				
200,000	.00352	.70	.26611	.71
1,000,000	.00339	.68	--	--
2,000,000	.00324	.65	.24715	.66
4,000,000	.00292	.58	--	--
8,000,000	.00230	.46	--	--

1/ Drums under control conditions and all tanks vertical cylindrical, filled to capacity.

2/ In red AOCS units with initial color of 4.02.

3/ Regression coefficient taken from table 9 (appendix) for drums. Regression coefficient according to formula 10 for tanks.

4/ In meq./kg. (AOCS), assuming initial peroxide value of 0.

5/ According to data taken from table 13 (appendix).

#### MINIMIZING CHANGE IN CHARACTERISTICS DURING STORAGE

The optimum conditions to minimize changes in the characteristics of cottonseed oils during storage in field tanks may be summarized as follows:

1. Colder areas are preferable because the characteristics of oils stored at lower temperature may change as much as 40 percent less than those of oils stored at higher temperature, (Time-Temperature Factor, page 2).
2. Large tanks should be used. There can be as much as 35 percent less rate of change in filled tanks of 8 million pounds' capacity as compared to tanks of 200,000 pounds' capacity (table 3).
3. Data indicate that there should be more change in oil characteristics (up to 25 percent in small tanks around 200,000 pounds' capacity) when tanks are not completely filled. Change should be less in large tanks of oil (capacities around 8 million pounds, table 10, appendix).
4. Data of oil in drums indicate that tanks of oil held at room temperature should show less change (up to 10 percent) than tanks of oil exposed to outside conditions (tables 9, 13 and 14, appendix).

5. Oils stored in drums without breathers showed much less increase in peroxide value and less decrease in color change. Tanks of oil with less access to air (but, perhaps, not under pressure) should show less change in most characteristics (tables 9, 13 and 14, appendix).

6. The use of vertical cylindrical tanks, rather than horizontal cylindrical or rectangular tanks (especially in the smaller capacities), should minimize change in the oil, with decreases as great as 25 percent (tables 11 and 12, appendix).

7. Because conditions such as drums painted black, addition of iron filings, or citric acid, etc. did not significantly affect the rate of change for most characteristics of oils stored in drums, it may be assumed that these factors would not affect oil stored in field tanks (table 9, appendix).

Conditions which would minimize changes in characteristics of crude oils are necessary even for minimum periods of storage.

Minimizing changes in characteristics for the long-term storage of refined oils may or may not be desirable depending on the initial characteristics of the oil and the effect of the various characteristics on quality and value, for example:

1. Moisture and volatile matter:

If refined oils contain more than 0.10 percent moisture and volatile matter, desirable conditions should maximize change, otherwise storage conditions are unimportant. Free water, however, can cause rapid increases in free fatty acids, especially in the bottom of tanks (fig. 1).

2. Free fatty acids:

Except when free fatty acids are unusually high or when free water is present, conditions of storage have little effect on changes of free fatty acids from a quality or value standpoint (fig. 2).

3. Refined oil color:

Because the color of all refined oil decreases during storage and because maximum colors are specified for all grades, conditions which would maximize change are desirable, providing the initial color was above 7.6 (figs. 3 and 4).

4. Bleached oil color:

Oils can be downgraded from bleachable or upgraded to bleachable depending on conditions of storage and initial relationship of refined and bleached colors. Whether conditions of storage should maximize or minimize change depends on the initial bleached color and the relationship of initial colors (figs. 7, 8 and 9).



## 5. Peroxide value:

Peroxide value provides a reliable measure of past conditions of storage (fig. 12). Although there are no specifications in the rules of the NCPA concerning peroxide value, the vegetable-oil industry objects to high PV oils and can claim "off flavors and odors" in such oils. The relation of the peroxide values of refined oils to the quality and shelf-life of shortenings processed from these oils will be discussed later.

## EVALUATION OF STORED OILS

### Refined Oils

#### Evaluation by Judges in Industry

During the fall of 1957 and again a year later, eight samples of the refined oils stored in drums were judged by members of industry who supplied the oils for the project. Most of the 46 judges who made the first examination also made the second examination, where 39 reports are summarized. The oils were judged for "flavor and odor" and prices were placed on those oils, which, in the opinion of the judges, did not meet this specification of the trading rules (NCPA) (table 4, appendix). (Shortenings were prepared from three of these oils in 1959. Evaluation of these shortenings will be discussed later.) There appeared to be little relation between the number of times an oil was judged "off in flavor and odor" and the age of the oil, the type of storage conditions, the objective analyses made for "keeping quality," or the estimated prices placed on the oils.

The range of the estimated discounts made on the "off" oils were on the average generally less than 1/2 cent per pound on oil valued on a 14 cents per pound market and, when averaged for all the graders, the variation was generally less than 1/10 cent.

Industry seldom grades freshly refined oils for "flavor and odor" and no agreement could be expected in grading oils that had been stored longer than usual. The data show this disagreement. However, there was some general agreement in the judgments of the same oil, both in 1957 and 1958 (when stored under three types of storage conditions), where there were large differences in the objective tests. This may be shown more clearly by comparing some of the data from table 4 (table 5, appendix).

Samples 2, 3 and 4 were from the same oil which was initially quite similar to oil in drums 11, 12 and 13. When these two oils, having similar characteristics, initially were judged, most of the judges seemed to differentiate among the oils which objective tests indicated had changed markedly during storage.

Agreement was not as good in judging samples of the same oil (under control conditions) examined in 1957 and in 1958 (table 6, appendix). These



data indicate that the judges placed a higher value on the same oils after 11 months' additional storage, even though there were significant increases in peroxide value during this period.

### Evaluation of Shortenings Made from Stored Oils

Four of the oils stored for 4 years and one oil stored for 1 1/4 years were used to prepare shortenings and the shortenings were compared with a shortening made from freshly refined oil.

The five stored oils were laboratory re-refined (80-percent, Max. 14°, Be' lye), washed with water and vacuum dried. The six oils, including the freshly refined oil, were then bleached (using 2-percent bleaching clay); hydrogenated; formulated to shortening consistency, using 9- to 11-percent cottonseed stearine gamma (standard hard stock); deodorized; and votated into plastic shortenings.

Analyses were made of quality factors which might indicate keeping quality (table 7, appendix). Four flavor- and odor-panel members could detect no distinct differences among the shortenings prepared from the various oils. All the shortenings were judged to have choice flavor and to have good odor when heated to 150° C.

A set of the six cans of shortening were opened just after preparation and held at room temperature with the lid replaced but not sealed, simulating household conditions. They were sampled periodically during an 8-month period (table 7, appendix). All six of the shortenings were judged to have good flavor and odor at the end of 8 months, with no distinguishable difference among samples. The shortening made from fresh oil, however, showed the least increase in peroxide value during the test period, but, in view of the flavor tests, this difference from the other shortenings cannot be called significant. Peroxide values of the stored refined oils did not appear to be related to the peroxide values of the 8-month old shortenings made from these oils. Color of the refined stored oils did not appear to be related to the color of shortenings prepared from these oils.

Tables 15, 16 and 17 (appendix) give detailed data of examinations made during the preparation of the shortenings.

The low tocopherol content of the stored oils compared to the freshly refined oil (table 15, appendix) should be noted, indicating loss of "resistance to oxidation" by lesser amounts of this antioxidant. This is confirmed in table 17 (appendix) by the lower AOM fat stabilities of the shortenings made from the stored oils as compared to that of the shortening made from fresh oil.

Data in the report (table 3) indicate that refined oils in filled tanks containing from 200,000 up to 8 million pounds of oil could test from 50 to 75 in peroxide value after 3 to 4 years storage (300 time-temperature units), depending on location. The stored oils in drums which were used for the shortenings showed peroxide values in this range.

Even if these oils were graded as PBSY under trading rules, such high PV values would require re-refining of the oils and the cost of re-refining would be taken into account in trading as a part of a discount below market quotation for PBSY. (Such high PV oils could be declared "off in flavor and odor" by the buyer.)

### Crude Oils

#### Relation of Initial Characteristics

In order to illustrate change in value of crude cottonseed oils in storage, it is necessary to first arrive at the most probable relationship between the initial characteristics. The three characteristics: refined color, free fatty acids, and refining loss, determine settlement values according to the trading rules (NCPA). The initial relationships between free fatty acids and both refined color and refining loss are highly significant.

Correlations between these initial characteristics of the eight crude oils in the project are shown in figures 15 and 16. Relationships of greater significance, however, can be shown by using the data of Whitten 13/ where analyses were made on all lots of crude oil produced under the official grading method for cottonseed of the U. S. Dept. Agr. in 10 states during the years 1942-46. These formulas and the formulas of Bailey and Barrow-Agee 14/ are shown in figures 15 and 16.

The Whitten curves are similar to those of Bailey and Barrow-Agee, the principle difference being that the Whitten curves of both refined color and refining loss show somewhat higher values for the same free fatty acids. The Whitten formulas are used in the following calculations for change in value of crude cottonseed oils during storage.

The Whitten observations on refined color have been reversed to derive a formula to determine the content of free fatty acids from refined color. This formula is as follows:

$$\text{FFA} = .74406 \text{ RC} - 2.95357$$

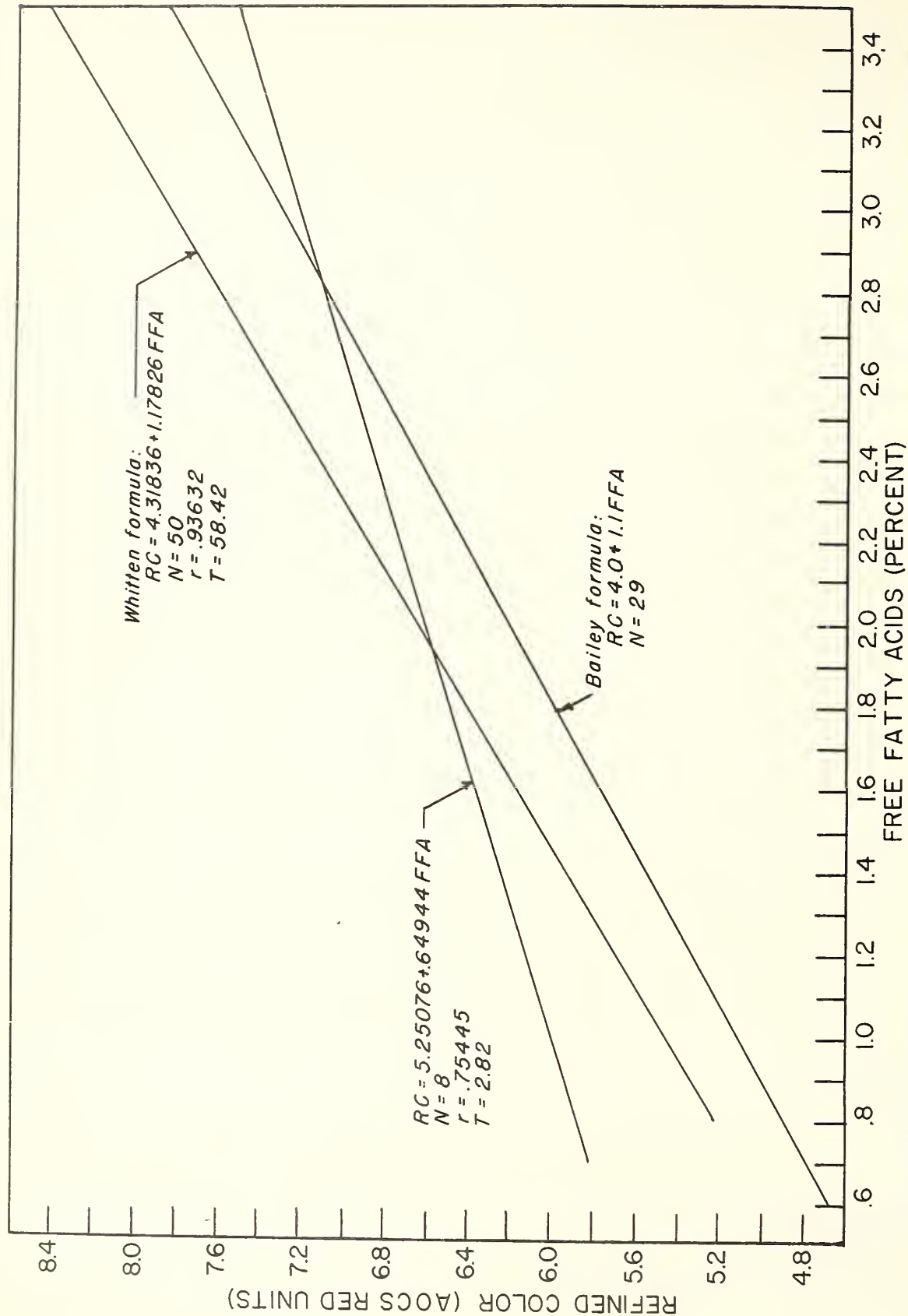
#### Change in Value During Storage

Figure 17 illustrates probable changes in settlement values for crude oils extracted by different methods and stored in drums, when initial refined

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13/ M. E. Whitten. The Grading of Cottonseed. U. S. Dept. Agr., PMA, Bul. 39, 61-65 pp. May 1951.

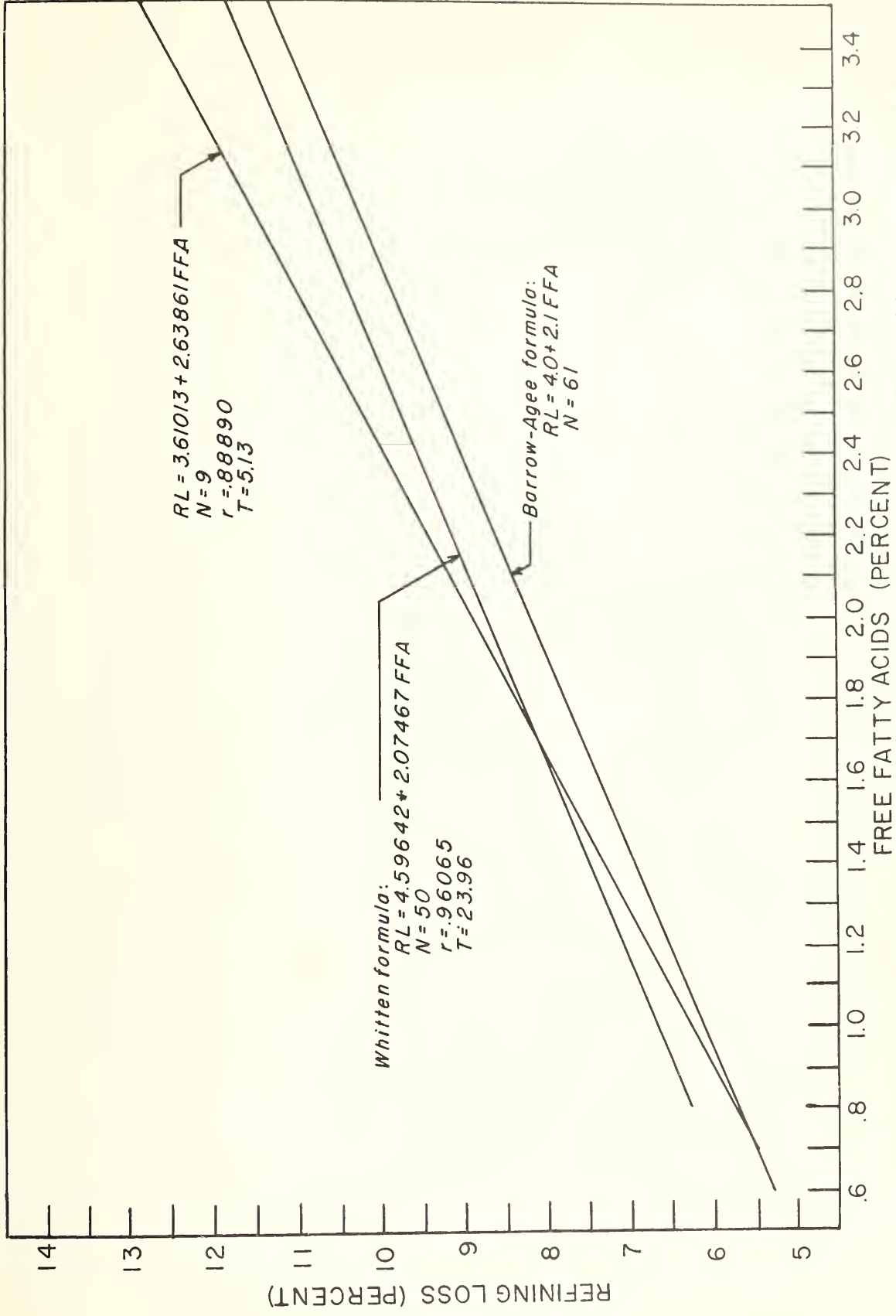
14/ A. E. Bailey. Cottonseed and Cottonseed Products. Interscience Publishers, Inc., New York. 1948.



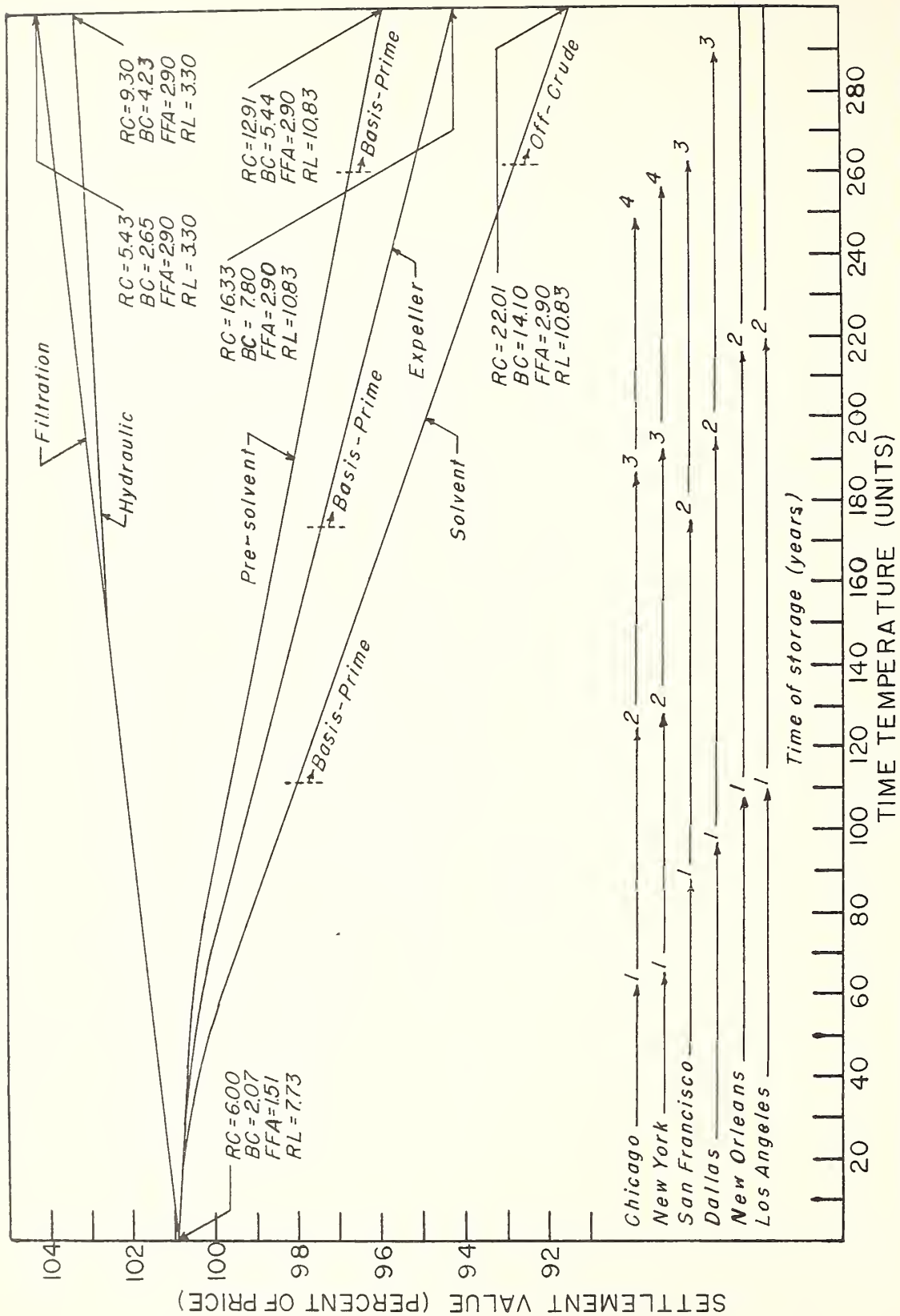
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Figure 15.--Relation of initial free fatty acids to initial refined color of crude cottonseed oils.



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 Figure 16.--Relation of initial free fatty acids to initial refining loss of crude cottonseed oils.



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Figure 17.--Settlement value of stored crude cottonseed oils--initial refined color of 6.0 red and initial bleached color of 2.07 red--related to time-temperature factor--stored in drums at six locations.



color is 6.00 (prime crude). The initial characteristics have been calculated from the following formulas:

$$\begin{aligned} \text{BC} &= .39108 \text{ RC} - .28048 \text{ (fig. 6)} \\ \text{FFA} &= .74406 \text{ RC} - 2.95357 \text{ (fig. 15)} \\ \text{RL} &= 4.59642 + 2.07467 \text{ FFA (fig. 16)} \end{aligned}$$

Change during storage, classed by extraction method, was calculated by the following formulas:

Filtration-extraction:

$$\begin{aligned} \text{Refined color,} & \quad Y = 6.00 - .00190 X \\ \text{Bleached color,} & \quad Y = 2.066 + .00195 X \\ \text{Free fatty acids,} & \quad Y = 1.51079 + .00464 X \\ \text{Refining loss,} & \quad Y = 7.73081 - .01477 X \end{aligned}$$

Hydraulic:

$$\begin{aligned} \text{Refined color,} & \quad Y = 6.00 + .01101 X \\ \text{Bleached color,} & \quad Y = 2.066 + .00721 X \\ \text{Free fatty acids,} & \quad Y = 1.51079 + .00464 X \\ \text{Refining loss,} & \quad Y = 7.73081 - .01477 X \end{aligned}$$

Prepress-solvent:

$$\begin{aligned} \text{Refined color,} & \quad Y = 6.00 + .02305 X \\ \text{Bleached color,} & \quad Y = 2.066 + .01126 X \\ \text{Free fatty acids,} & \quad Y = 1.51079 + .00464 X \\ \text{Refining loss,} & \quad Y = 7.73081 + .01033 X \end{aligned}$$

Expeller:

$$\begin{aligned} \text{Refined color,} & \quad Y = 6.00 + .03443 X \\ \text{Bleached color,} & \quad Y = 2.066 + .01912 X \\ \text{Free fatty acids,} & \quad Y = 1.51079 + .00464 X \\ \text{Refining loss,} & \quad Y = 7.73081 + .01033 X \end{aligned}$$

Solvent:

$$\begin{aligned} \text{Refined color,} & \quad Y = 6.00 + .05338 X \\ \text{Bleached color,} & \quad Y = 2.066 + .04010 X \\ \text{Free fatty acids,} & \quad Y = 1.51079 + .00464 X \\ \text{Refining loss,} & \quad Y = 7.73081 + .01033 X \end{aligned}$$

as shown in figures 2, 5, 10 and 14.

If the relationship for rate of change in characteristics of crude oils between drums and tanks is used as shown in table 3 for refined oils, the changes in value as shown in figure 17 would be approximately 50 percent in 8-million-pound tanks of oil.

Table 4.--Summaries of judges' reports in grading stored refined cottonseed oils for "off-flavor and odor," relation to specified laboratory tests, and average estimated evaluations 1/

Sample number	Type of storage <u>2/</u>	Method of extraction	Time in storage:	Judges reporting "off" oil	Laboratory tests			Judges who would discount "off" oil	Average estimated price of oils per pound		
					Pct.	Meq./kg.	Hr.		No.	Pct.	Ct.
			No.								
2	No breather - outside	Solvent <u>7/</u>	28	5	11	30	10	10	13.46	13.94	
3	Breather - outside	Solvent <u>7/</u>	28	7	15	76	6	8	13.80	13.99	
1	Breather - inside	Solvent <u>7/</u>	28	12	26	41	9	10	13.75	13.98	
6	Breather - outside	Expeller	10	14	30	26	10	14	13.29	13.94	
5	Sealed - outside	Solvent <u>7/</u>	28	16	35	76	2	7	13.60	13.95	
4	Breather - one-half filled:										
	- outside	Solvent <u>7/</u>	28	17	37	172	0	6	13.13	13.91	
7	Breather - outside	Expeller	10	20	43	22	11	13	13.69	13.97	
8	Breather - outside	Prepress solvent:	10	30	65	27	11	13	13.52	13.91	
12	No breather - outside	Solvent <u>8/</u>	39	7	18	15	15	11	13.79	13.99	
17	Breather - outside	Expeller	21	7	18	52	11	12	14.00	14.00	
15	Breather - outside	Expeller	22	15	38	62	10	10	13.79	13.99	
18	Breather - outside	Prepress solvent:	21	17	44	68	10	13	13.88	13.99	
14	(Fresh oil)	Screw press	0	17	44	3	19	--	13.81	13.98	
11	Breather - one-half filled:										
	- outside	Solvent <u>8/</u>	39	17	44	160	0	7	13.37	13.86	
13	Breather - outside	Solvent <u>8/</u>	39	18	46	103	4	8	13.58	13.91	
16	Breather - outside	Filtration-									
	- extraction		21	26	67	43	10	13	13.62	13.91	

1/ 12 mills and refineries supplied oil for the project and 2 laboratories made tests. Workers in these organizations graded and evaluated the oils. Samples 1 through 8 were examined in the fall of 1957 and samples 11 through 18 were examined in the fall of 1958.

2/ Oil was stored in drums painted aluminum at Beltsville, except as noted.

3/ Peroxide value tested by Laboratory "A" according to AOCs methods.

4/ According to AOCs methods, except end-point determined organoleptically and by "break" in peroxide value.

5/ Tested by Laboratory "A".

6/ Estimated from tests made before deodorization, by Laboratory "B".

7/ Oil from same lot at refinery prior to storage.

8/ Oil from same lot at different refinery, prior to storage.



Table 6.--Summary of judges' reports in grading three stored refined cottonseed oils, each taken twice from storage, for "off-flavor and odor," relation to specified laboratory tests, and average estimated evaluations 1/

Sample number	Method of extraction	Time in storage	Judges reporting oil "off"	Laboratory tests	Judges who would discount "off" oil	Average estimated price of oils per pound				
		Mo.	No.	Pct.	Meq./kg.	Hr.	No.	Pct.	Ct.	Ct.
6	:Expeller	: 10	: 14	: 30	: 26	: 10	: 4	: 9	: 13.29	: 13.94
15	:Expeller	: 22	: 15	: 38	: 62	: 10	: 2	: 5	: 13.79	: 13.99
7	:Expeller	: 10	: 20	: 43	: 22	: 11	: 4	: 9	: 13.69	: 13.97
17	:Expeller	: 21	: 7	: 18	: 52	: 11	: 0	: 0	: 14.00	: 14.00
8	:Prepress-solvent	: 10	: 30	: 65	: 27	: 11	: 9	: 20	: 13.52	: 13.91
18	:Prepress-solvent	: 21	: 17	: 44	: 68	: 10	: 3	: 8	: 13.88	: 13.99

1/ Data taken from table 4.

Table 7.--Color, peroxide value, and AOM fat stability of specified stored and freshly refined cottonseed oils, before and after re-refining and bleaching, and when made into shortenings 1/

Source of samples	Color <u>2/</u>						Peroxide value <u>3/</u>						AOM fat stability <u>4/</u>					
	Drum number <u>5/</u>						Drum number <u>5/</u>						Drum number <u>5/</u>					
	12 :	20 :	16 :	19 :	91 :	6/ :	12 :	20 :	16 :	19 :	91 :	6/ :	12 :	20 :	16 :	19 :	91 :	6/ :
Refined oils--prior to shortening process .....	2.8	3.0	2.9	3.6	9.4	6.2	256.0	117.0	76.0	15.0	44.0	4.0	0	3	9	10	7	--
Re-refined and bleached oils .....	1.0	1.2	1.2	1.4	2.3	2.1	115.0	56.0	43.0	10.0	20.0	2.8	--	--	--	--	--	--
Shortenings:																		
Shortenings freshly made.....	1.1	.8	.9	.7	1.7	1.8	.6	.4	.4	.4	.4	.3	47	43	40	48	43	67
Shortenings in sealed can -																		
1/2 month .....	1.2	.8	1.0	.7	2.0	1.6	1.3	.9	.7	.8	.9	1.0	49	45	43	52	46	55
Shortenings in "opened can"																		
2 months <u>7/</u> .....	2.0	1.3	1.6	1.3	2.8	2.4	2.5	3.2	2.3	2.5	1.8	.8	--	--	--	--	--	--
Shortenings in "opened can"																		
3 months <u>7/</u> .....	2.0	1.5	1.8	1.5	2.4	2.3	6.1	7.7	4.2	3.9	4.7	3.4	--	--	--	--	--	--
Shortenings in "opened can"																		
5 months <u>7/</u> .....	--	--	--	--	--	--	10.3	14.0	13.3	12.6	15.2	7.0	--	--	--	--	--	--
Shortenings in "opened can"																		
8 months <u>7/</u> .....	2.1	1.3	1.3	1.2	2.1	2.0	19.0	23.0	22.0	17.0	19.0	10.0	--	--	--	--	--	--

1/ See tables 15, 16, and 17 (appendix) for other examinations made at time of preparation of shortenings.

2/ In red units according to AOCS.

3/ In meq./kg. according to AOCS.

4/ In hours according to AOCS.

5/ Conditions of stored drums as follows:

Number 12 = Half-filled, painted aluminum with breather, outside 4 years at Beltsville, Md.

Number 20 = Painted aluminum with breather, outside 4 years at Beltsville, Md.

Number 16 = Stored inside, with breather, 4 years at Beltsville, Md.

Number 19 = Painted aluminum, without breather, outside 4 years at Beltsville, Md.

Number 91 = Painted aluminum, with breather, outside 1 1/4 years at Bayonne, N. J.

6/ Freshly refined oil--not re-refined prior to bleaching.

7/ Held at room temperature--lid replaced between sampling, but not sealed.



Table 8.--Factors for correlation of the relationships of characteristics between the two laboratories 1/

Characteristics		Correlation factors				
Independent variable-- Laboratory "B"	Dependent variable-- Laboratory "A"	Regression coefficient: <u>2/</u>	Y - intercept: <u>3/</u>	Coefficient of correlation: <u>4/</u>	Standard error of estimate: <u>5/</u>	
<u>X</u>	<u>Y</u>	<u>b</u>	<u>a</u>	<u>r</u>	<u>S<sub>y.x</sub></u>	
Moisture and volatile matter...	Moisture and volatile matter	0.8121	-0.0010	0.9497	0.0374	
Free fatty acids...	Free fatty acids	.9885	- .0124	.8602	.0204	
Refined color.....	Refined color	1.1444	- .6428	.9864	.3759	
Bleached color.....	Bleached color	1.0813	- .2115	.9647	.2587	
Peroxide value.....	Peroxide value	.7775	5.9752	.9506	10.9022	
Peroxide value.....	AOM fat stability:	- .0638	12.4914	- .9129	1.2254	

1/ Laboratory "B" analyzed about 15 percent of the samples from each of the drums, whereas Laboratory "A" analyzed the others. The correlation factors were used to estimate the analyses made by Laboratory "B" in terms of Laboratory "A". The relationships shown are based on 32 duplicate samples analyzed by each laboratory.

2/ Change in characteristics of Laboratory "A" for every unit change of Laboratory "B".

3/ Estimated difference of any test between laboratories in addition to unit change.

4/ The degree of relationship of the characteristics between the laboratories. Perfect relationship equals 1.

5/ About one-third of the estimates of the observations vary above or below the average estimate by this amount.

Table 9.--Correlation factors of the relationship between time-temperature and color of similar refined cottonseed oils stored under various conditions 1/

Drum no.	Type of storage conditions <u>2/</u>	Total time- tempera- ture units <u>3/</u>	Obser- vations <u>4/</u>	Refined color <u>5/</u>			Significance of correlation <u>8/</u>
				Initial	Regres- sion coeffi- cient <u>6/</u>	Standard error of estimate of b <u>7/</u>	
<u>9/</u>		<u>T-T</u>	<u>N</u>	<u>a</u>	<u>b</u>	<u>S<sub>b</sub></u>	<u>T</u>
	Controls and other <u>10/</u> .....	304	150	3.98667	-0.00502	0.00021	23.90
4,19	No breathers <u>11/</u>	290	22	3.93230	- .00375	.00071	5.28
15	No breather <u>12/</u>	280	4	3.76221	- .00384	.00275	1.40
2,16	Stored inside <u>13/</u>	290	24	4.41284	- .00567	.00065	8.72
24,26	Stored inside <u>14/</u>	435	28	3.90357	- .00395	.00024	16.46
7,8	Half-filled <u>15/</u>						
12,13		290	44	4.06818	- .00669	.00051	13.12

1/ There were no significant differences between the two oils refined in miscella in the rate of color decrease. Correlations as in 9/ were grouped.

2/ Drums painted aluminum with breathers and exposed to outside atmospheric conditions, except as noted.

3/ In 100 "accelerated" hour-degrees. See table 1.

4/ Number of samples taken and tested.

5/ In AOCS red units.

6/ Change in color for every time-temperature unit. Minus sign indicates decrease.

7/ The amount of the variation above and below the regression coefficient in about one-third of the observations.

8/ A measure of significance of the correlation =  $b/S_b$ .

9/ Drums numbered 1, 3, 5, 6, 9, 10, 11, 14, 17, 18, 20, 23 and 25.

10/ Includes 4 controls, 2 drums painted black, 2 drums with added water, 1 with iron filings, 1 with food liner, 1 fogged with mineral oil, 1 with citric acid and 1 was agitated at sampling.

11/ There was no significant difference in the rate of color decrease from the controls (9/). Drums were opened only when sampled.

12/ The rate of color decrease was not significantly different from controls. This drum was opened only on 7/14/55, 10/11/57, 7/23/58 and 4/23/59. Oil was under pressure at time of each opening.

13/ No significant difference in rate of color decrease from controls. These drums were stored at Beltsville.

14/ The rate of color decrease was significantly different from the controls and also from the same oils at Beltsville. These drums were stored at New Orleans; however, were probably colder in the winter months than the drums under 13/.

15/ Included the half-filled drums and the half-filled drums containing iron filings. The rate of color decrease was significantly different from the controls.

Table 10.--Summary of data used to estimate differences between rates of color decrease of stored refined cottonseed oils in partially filled vertical cylindrical tanks compared to data for filled tanks

Tank no..	Quantity of oil	Quantity of fill	Color $\bar{1}/$		Significance of correlation $\frac{3}{\bar{3}}$	Color $\bar{1}/$		Ratio of b to b"
			Initial	Regression coefficient $\frac{2}{\bar{2}}$		b adjusted to a $\frac{4}{\bar{4}}$	b' adjusted to quantity of oil $\frac{5}{\bar{5}}$	
	Pounds	Percent	$\bar{a}$	$\bar{b}$	$\bar{T}$	$\bar{b}'$	$\bar{b}''$	
13	243,284	73	6.88673	-0.00602	$\frac{6}{\bar{6}}$ 1.24	-0.00798	-0.00805	.75
14	240,450	72	6.59786	- .00282	$\frac{6}{\bar{6}}$ .53	- .00753	- .00760	.37
5	5,035,700	59	8.30787	- .00809	$\frac{6}{\bar{6}}$ 1.76	- .01021	- .00811	1.00
28	261,420	41	6.33971	- .00816	9.17	- .00712	- .00718	1.14
134	60,300	33	7.00329	- .01053	11.08	- .00817	- .00831	1.27
51	75,500	22	7.53026	- .01156	7.50	- .00899	- .00914	1.27

1/ Color in AOCS red units.

2/ Decrease in color for every time-temperature unit.

3/  $T = b/\bar{S}_b$ , see table 9, footnote 8/.

4/ The regression coefficient (b) adjusted to the initial color (a) according to:  $b' = .00283 - .00157a$ .

5/ The regression coefficient further adjusted to take into account the quantity of oil if in a tank filled to capacity according to the formula:  $b'' = 102 - .00449 (b/b')$ .

6/ Not statistically significant for 19 times out of 20 observations (the 5-percent confidence level).

Table 11.--Summary of data used to estimate differences between rates of color decrease of refined cotton-seed oils stored in horizontal cylindrical tanks compared to data for vertical cylindrical tanks\*

Tank no.	Quantity of oil	Quantity of fill	Color $\bar{1}/$		Significance of correlation $\frac{3}{2/}$	Color $\bar{1}/$		Ratio of b to b''
			Initial	Regression coefficient $\frac{2/}{2/}$		b adjusted to a $\frac{4/}{4/}$	b' adjusted to quantity of oil $\frac{5/}{5/}$	
	<u>Pounds</u>	<u>Percent</u>	<u>a</u>	<u>b</u>	<u>T</u>	<u>b'</u>	<u>b''</u>	
100	175,560	97	5.84065	-0.00775	5.31	-0.00634	-0.00643	1.21
101	172,823	96	6.11131	- .00742	5.80	- .00676	- .00684	1.08
102	170,880	95	7.04911	- .00989	10.63	- .00824	- .00834	1.19
103	172,376	95	7.06471	- .00968	6.45	- .00826	- .00844	1.15

\*See table 10 for footnotes.

Table 12.--Summary of data used to estimate differences between rates of color decrease of refined cotton-seed oils stored in rectangular tanks compared to data for vertical cylindrical tanks\*

Tank no.	Quantity of oil	Quantity of fill	Color 1/		Significance of correlation 3/	Color 1/		Ratio of b to b''
			Initial	Regression coefficient 2/		b adjusted to a 4/	b' adjusted to quantity of oil 5/	
	<u>Pounds</u>	<u>Percent</u>	<u>a</u>	<u>b</u>	<u>T</u>	<u>b'</u>	<u>b''</u>	
1,103	339,160	91	7.32465	-0.01034	5.44	-0.00867	-0.00877	1.19
1,102	336,920	90	7.38275	- .01040	6.27	- .00876	- .00880	1.18
1,104	329,680	88	7.92052	- .01292	11.64	- .00961	- .00966	1.34
1,101	241,180	64	6.96117	- .01009	7.95	- .00810	- .00817	1.24

\*See table 10 for footnotes.

Table 13.--Summary of data showing differences in peroxide values, among refined cottonseed oils in control and other drums under specified storage conditions and in field tanks

Type of storage conditions <u>1/</u>	Total time-temperature: units <u>2/</u>	Observations <u>3/</u>	Peroxide value <u>4/</u>		Significance of correlation <u>7/</u>
			Regression coefficient <u>5/</u>	Standard error of estimate of b <u>6/</u>	
	<u>T-T</u>	<u>N</u>	<u>b</u>	<u>S<sub>b</sub></u>	<u>T</u>
Drums:					
Controls and other conditions .....	300	392	0.37314	0.00670	55.69
One-half filled:	310	48	.55644	.04635	12.01
Inside.....	310	56	.20252	.00767	26.40
No breather--in: sun.....	263	33	.11357	.01781	6.37
No breather--no: sun.....	188	18	.05011	.01199	4.18
Field tanks:					
Controls <u>8/</u> .....	100	<u>9/</u> 18 <u>10/</u>	.26611	--	--
Experimental tank <u>11/</u> .....	76	10	.24715	.01915	12.91

1/ Drums painted aluminum, with breathers, stored outside, except as noted.

2/ In 100 "accelerated" hour-degrees. See table 1.

3/ Number of samples taken and tested.

4/ In meq./kg. according to AOCS.

5/ Increase in peroxide value for every time-temperature unit. Initial peroxide value assumed to be 0.

6/ The amount of variation above and below the regression coefficient in about one-third the observations.

7/ A measure of significance of the correlation =  $b/S_b$ .

8/ Samples from balance and bottom of tanks numbered 60, 62, 135, 136, 137, 138, 139, 140 and 141. Average oil in tanks was 202,575 pounds.

9/ Only one set of samples taken.

10/ Average of the 18 samples, with a standard deviation of 4.

11/ Vertical cylindrical tank containing 2,031,148 pounds of oil.



Table 14.--Summary of data showing differences in AOM fat stabilities among refined cottonseed oils in control and other drums under specified storage conditions and in field tanks

Type of storage conditions <u>1/</u>	Total time-temperature units <u>2/</u>	Observations <u>3/</u>	AOM fat stability <u>4/</u>		Significance of correlation <u>7/</u>
			Regression coefficient <u>5/</u>	Standard error of estimate of b <u>6/</u>	
	<u>T-T</u>	<u>N</u>	<u>b</u>	<u>S<sub>b</sub></u>	<u>T</u>
Drums:					
Controls and other conditions.....	300	392	-0.03541	.00094	37.67
One-half filled. Inside.....	310	48	<u>8/-</u> .04147	.01274	3.26
No breather--in sun.....	310	56	- .02151	.00118	18.23
No breather-no sun.....	263	33	<u>9/-</u> .01113	.00375	2.96
	188	18	<u>9/</u> .01022	.00682	1.50
Field tanks:					
Controls <u>10/</u> ....	100	<u>11/</u> 18	<u>12/</u> --	--	--
Experimental tank <u>13/</u> .....	76	10	<u>14/</u> .06022	.02387	2.52

1/ Drums painted aluminum, with breathers, stored outside, except as noted.

2/ In 100 "accelerated" hour-degrees. See table 1.

3/ Number of samples taken and tested.

4/ Not in accordance with methods of the AOCS. End-point was determined organoleptically and by "break" in peroxide value instead of the use of 100 PV as an end-point. See "Relation of Peroxide Value and AOM Fat Stability," p. 29.

5/ Decrease in AOM fat stability for every time-temperature unit. Initial AOM varied from 13 to 14 in drums and was 15.5 in experimental field tank.

6/ The amount of variation above and below the regression coefficient in about one-third the observations.

7/ A measure of significance of the correlation =  $b/S_b$ .

8/ Not significantly different from "controls and other conditions."

9/ Not significantly different from each other, but when all "no breather" drums are grouped, is significantly different from "controls and other conditions."

10/ Samples from balance and bottom of tanks numbered 60, 62, 135, 136, 137, 138, 139, 140 and 141. Average oil in tanks was 202,575 pounds.

11/ Only one set of samples taken. 12/ Average AOM of the 18 samples after 100 time-temperature units was 6.2 with a standard deviation of 1.9, however AOM end-point was determined at 100 PV. The AOM should be about 4.5 hours longer when compared to methods used in the project. See figure 12. As no initial AOM's were available on these oils, no regression coefficient can be estimated. 13/ Vertical cylindrical tank containing 2,031,148 pounds of oil.

14/ Not significantly different from "controls and other conditions."

Table 15.--Analyses of stored refined cottonseed oils, before and after laboratory re-refining and bleaching

Sample number	After storage				After re-refining and bleaching 1/							
	Iodine number	Color	Free fatty acids	Peroxide value	Tocopherol gamma	Color	Peroxide value	Fatty acid composition 2/	Linoleic	Oleic	Saturated	
	Units	Units	Percent	Meq./kg.	Percent	Units	Meq./kg.	Percent	Percent	Percent	Percent	
1	103.9	2.8	0.05	256	0.010	1.0	115	44.0	26.9			24.7
2	104.6	2.9	.06	76	.016	1.2	43	43.7	28.4			23.5
3	110.7	9.4	.06	44	.029	2.3	20	49.1	24.3			22.2
4	104.7	3.6	.04	15	.024	1.4	10	44.4	26.9			24.3
5	104.8	3.0	.04	117	.014	1.2	56	44.5	26.9			24.2
3/6	107.6	6.2	.05	4	.036	2.1	2.8	47.2	24.6			23.8

1/ 2-percent bleaching clay.

2/ 95.6 percent TFA basis. AOCs Method Cd-7-48.

3/ Freshly refined cottonseed oil, not re-refined prior to bleaching.

Table 16.--Laboratory hydrogenation and analyses of cottonseed snows prepared from stored refined cottonseed oils after re-refining and bleaching

Analyses												
Sample number				Consistency						Fatty acid composition 1/		Hydro- genation time 2/
	Peroxide value	Iodine number	Melting point (Wiley)	Penetration	Dilatometric solids							
						60°F.	50°F.	70°F.	92°F.	Linoleic	Oleic	
	Meq./kg.	Units	°C.	Units	Pct.	Pct.	Pct.	Pct.	Pct.	Pct.	Minutes	
1	115	66.1	37.3	55	24.3	16.5	5.3	9.3	54.8	31.5	36	
2	43	72.6	35.1	85	19.5	12.3	2.8	14.3	51.9	29.4	24	
3	20	74.0	35.0	83	19.3	12.3	2.8	12.3	57.5	25.8	25	
4	10	71.1	36.0	75	21.0	13.3	3.5	14.3	50.3	31.0	21	
5	56	70.1	35.0	73	21.3	13.5	3.8	13.1	51.6	30.9	29	
3/6	2.8	70.9	35.3	62	22.0	13.8	3.3	11.6	55.5	28.5	20	

1/ 95.6 percent TFA basis. AOCs Method Cd-7-48.

2/ Hydrogenation data--2,000-gram batch, 0.1 percent nickel, 0.4 percent dicalite 115 (Carrier); agitator at 3,000 r.p.m., 135° C., pure cylinder hydrogen atmospheric pressure, hydrogen flow--1.5-2.0 liters/min.

3/ Freshly refined oil.









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